(12) UK Patent Application (19) GB (11) 2 412 916 (13) A

(43) Date of A Publication 12.10.2005

(21) Application No: 0506757.4

(22) Date of Filing: 04.04.2005

(30) Priority Data:
(31) 04101455 (32) 08.04.2004 (33) EP
(31) 04105995 (32) 23.11.2004

(71) Applicant(s):
Ciba Speciality Chemicals Holding Inc
(Incorporated in Switzerland)
Klybeckstrasse 141, 4057 Basel,
Switzerland

(72) Inventor(s):
Victor Paul Eliu
Beate Fröhling
Dominique Kauffmann

(continued on next page)

(51) INT CL[7]:
C09B 43/40 , A61K 7/13 , C09B 26/04 43/00 43/11 43/136 44/08 49/04 49/06 49/12 67/02

(52) UK CL (Edition X):
C4P PZZ
U1S S1281 S1293 S1300 S1302 S1343 S1377 S1537 S1565

(56) Documents Cited:
WO 2003/099242 A1
X G H Crawshaw, "Proc. Int. Wool Text. Res. Conf., 8th (1990)", pub. 1990, Wool Res. Organ. N. Z., Christchurch, N. Z., Vol. 4, pages 177-186 & Chemical Abstracts, abstr no 118:170981.
Journal of the Society of Dyers and Colourists, 1991, Vol. 107(10), pages 357-362 & Chemical Abstracts, abstr no 117:9682.

(continued on next page)

(54) Abstract Title: **Sulphide & disulphide dyes for use in dyeing keratin-containing fibres**

(57) A method of dyeing keratin-containing fibers (such as wool and hair) comprises treating the fiber with at least one sulfide dye of formula

(1) $R_1-(Z_1)r-Y_1-S-Z_3-[-Y_2-(Z_2)q-R_2]_n$ [wherein

R_1 and R_2 each independently from each other are a residue of an organic dye;
Y_1 and Y_2 each independently from each other are unsubstituted or substituted, straight-chain or branched, interrupted or uninterrupted -C_1-C_{10}alkylene-; -C_5-C_{10}cycloalkylene-; C_5-C_{10}arylene; or-C_5-C_{10}arylene-(C_1-C_{10}alkylene)-;
Z_1 and Z_2 independently from each other are -C(O)-; -C_2-C_{12}alkenylene-; -$(CH_2CH_2-O)_{1-5}$-; -C_1-C_{10}alkylene(C_5-C_{10}arylene)-; -C_5-C_{10}arylene-; -C_5-C_{10}cycloalkylene-; -C(O)O-;

-OCO-; -N(R_3)-; $-\overset{R_3}{\underset{R_4}{N^+}}-$; -CON(R_4)-; -(R_5)NC(O)-; –O-; -S-; -S(O)-; or –$S(O)_2$-;

R_3,R_4 and R_5 are each independently from each other hydrogen; or unsubstituted or substituted, straight-chain or branched, monocyclic or polycyclic, interrupted or uninterrupted C_1-C_{14}alkyl; C_2-C_{14}alkenyl; C_6-C_{10}aryl; C_6-C_{10}aryl-C_1-C_{10}alkyl; or C_1-C_{10}alkyl(C_5-C_{10}aryl);
r, q and n independently from each other are 0 or 1,
if n is 0,
Z_3 is hydrogen; and
if n is 1,
Z_3 is -S-]
with the proviso that the method does not comprise treating the fiber with an enzyme of the type protein disulfidisomerase (EC 5.3.4.1).
Leather, silk, cellulose, polyamides (eg nylon) and cotton may likewise be dyed.
Further, there is disclosed compositions comprising dyes of formula (1) (especially comprising other dyes) and processes for the preparation of dyes of formula (1).
Certain dyes of formula (1) are claimed per se. Further compounds of formulae (35)-(38) as defined herein are also claimed per se.

GB 2 412 916 A

GB 2412916 A continuation

(74) Agent and/or Address for Service:
Ciba Speciality Chemicals Water Treatments Limited
Cleckheaton Road, Low Moor, BRADFORD,
West Yorkshire, BD12 0JZ,
United Kingdom

(56) cont
Dyes and Pigments, 1995, Vol. 29(4), pages 275-294 & Chemical Abstracts, abstr no 124:90240.
Journal of the Society of Dyers and Colourists, 1975, Vol. 91(8), pages 259-264 & Chemical Abstracts, abstr no 83:195191.

(58) Field of Search:
Other: **CAS ONLINE**

Sulfide dyes

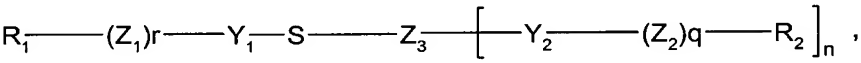
The present invention relates to novel sulfide dyes, compositions thereof, to processes for their preparation and to their use for the dyeing of organic materials, such as keratin fibers, wool, leather, silk, cellulose or polyamides, especially keratin-containing fibers, cotton or nylon, and preferably hair, more preferably human hair.

It is known, for example, from WO 95/01772 that cationic dyes can be used to dye organic material, for example keratin, silk, cellulose or cellulose derivatives, and also synthetic fibers, for example polyamides. Cationic dyes exhibit very brilliant shades. A disadvantage is their unsatisfactory fastness to washing.

R. S. Asquith, P. Carthew and T. T. Francis describe in JSDC from May 1973, pages 168-172 that ortho-azo disulfide dyes do not lead to covalent bonding with keartin fiber of wool, and that para-azo disulfide dyes underwent only at high concentration some covalent bindings with wool.

The actual technical problem of the present invention was to provide dyes that are distinguished by deep dying having good fastness properties with respect to washing, light, shampooing and rubbing.

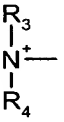
Accordingly, the present invention relates to a method of dyeing keratin-containing fibers, comprising treating the fiber with at least one sulfide dye of formula

(1)  , wherein

R_1 and R_2 each independently from each other are a residue of an organic dye;

Y_1 and Y_2 each independently from each other are unsubstituted or substituted, straight-chain or branched, interrupted or uninterrupted -C_1-C_{10}alkylene-; –C_5-C_{10}cycloalkylene-; C_5-C_{10}arylene; or-C_5-C_{10}arylene-(C_1-C_{10}alkylene)-;

Z_1 and Z_2 independently from each other are –C(O)-; -C_2-C_{12}alkenylene-; -$(CH_2CH_2-O)_{1-5}$-; -C_1-C_{10}alkylene(C_5-C_{10}arylene)-; –C_5-C_{10}arylene-; –C_5-C_{10}cycloalkylene-; -C(O)O-;

-OCO-; -N(R_3)-;  ; -CON(R_4)-: -(R_5)NC(O)-; –O-; -S-; -S(O)-; or –$S(O)_2$-;

R_3, R_4 and R_5 are each independently from each other hydrogen; or unsubstituted or substituted, straight-chain or branched, monocyclic or polycyclic, interrupted or uninterrupted C_1-C_{14}alkyl; C_2-C_{14}alkenyl; C_6-C_{10}aryl; C_6-C_{10}aryl-C_1-C_{10}alkyl; or C_5-C_{10}alkyl(C_5-C_{10}aryl);

r, q and n independently from each other are 0 or 1,

if n is 0,

Z_3 is hydrogen; and

if n is 1,

Z_3 is –S-;

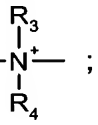
with the proviso that the method does not comprise treating the fiber with an enzyme of the type of a protein disulfidisomerase (EC 5.3.4.1).

Preferably Y_1 and Y_2 are unsubstituted or substituted straight-chain or branched interrupted or uninterrupted ~~or~~ –C_5-C_{10}cycloalkylene- or -C_1-C_{10}alkylene.

Further preferred is the method of the present invention, wherein Disulfid-dyes are used, i.e. wherein in formula (1) n is 1.

More preferred is the method of the present invention, wherein R_1 and R_2 are identical.

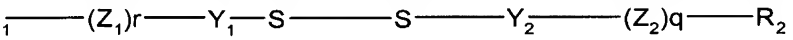
Further more preferred is the method of the present invention, wherein

Z_1 and Z_2 independently from each are other -N(R_3)-;  ; -CON(R_4)-; -(R_5)NC(O)-; -O-;

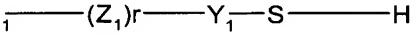
or -S-; and

R_3, R_4 or R_5 are defined as in formula (1)

Further more preferred is the method wherein at least one sulfide dye of formula

(2) 

and/or at least one sulfide dye of formula

(3) 

is used, wherein

R_1, R_2, Z_1, Z_2, Y_1, Y_2, r and q are defined as in formula (1).

Further more preferred is the method of the present invention, wherein the residue of an organic dye is selected from the group of anionic, cationic, neutral, amphoter and zwitterionic dyes, and especially preferred, wherein the residue of an organic dye is a cationic dye.

Furthermore preferred is the method of the present invention, wherein the residue of an organic dye is selected from the group of anthraquinone, acridine, azo, azomethine, hydrazomethine, benzodifuranone, coumarine, diketopyrrolopyrrol, dioxaxine, diphenylmethane, formazan, indigoid, indophenol, naphthalimide, naphthoquinone, nitroaryl, merocyanine, methin, oxazine, perinone, perylene, pyrenequinone, phtalocyanine, phenazine, quinoneimine, quinacridone, quinophtalone, styryl, triphenylmethan, xanthene, thiazine and thioxanthene dye.

Preferably the residue of an organic dye is selected from azo, azomethin, hydrazomethin, merocyanine, methin and styryl dyes, and more preferred from azo, azomethin dye and hydrazomethin dyes;

Suitable nitroaryl dyes of the present invention are for example selected from the following compounds:
4-amino-1-nitrobenzene, 2-amino-6-chloro-4-nitrophenol, 2-amino-3-nitrophenol, 2-amino-1-nitrobenzene, 1,4-diamino-2-nitrobenzene, 4-acetylamino-1-amino-2-nitrobenzene, 1,2-diamino-4-nitrobenzene, 1-amino-2-methyl-6-nitrobenzene, 3-amino-6-methylamino-2- nitropyridine (Azarot), pikraminacid, 4-amino-3-nitrophenol, 4-amino-2- nitrophenol, 6-nitro-o-toluidine, 1, 4-bis- (2-hydroxyethyl) amino-2- nitrobenzene, 1- (2-hydroxyethyl) amino-2-nitrobenzene (HC Yellow No. 2), 1- (2-hydroxyethyl) amino-2- (2-hydroxyethyl) oxy-4-nitrobenzene (HC YellowNo. 4), 1-amino-2- (2-hydroxyethyl) amino-5-nitro-benzene (HC YellowNo. 5), 1- (2, 3-dihydroxypropyl) amino-4-trifluormethyl-2-nitro-benzene (HC Yellow No. 6), 1- (2-hydroxyethyl) amino-4-chlor-2-nitro-benzene (HC Yellow No. 12), 1-amino-2-nitro-4-[bis (2-hydroxyethyl)] amino-benzene (HC Red No. 13), 4-chloro-2, 5-bis [(2, 3-dihydroxypropyl) amino]-1-nitro-benzene (HC Red No. 11), 1-amino-5-chloro-4-(2, 3-dihydroxypropyl) amino-benzene (HC Red No. 10), 1-amino-2-nitro-4- (2-hydroxyethyl) amino-benzene (HC Red No. 7), 2-chloro-5-nitro-N-(2-hydroxyethyl)-1, 4-phenylendiamine, 1-[(2- hydroxyethyl)-amino]-2-nitro-4-amino-benzene (HC Red No. 3), 4-amino-2- nitrodiphenylamine (HC Red No. 1), 2-nitro-4'-hydroxy-diphenylamine (HC Orange No. 1), 1-amino-3-methyl-4-(2-hydroxyethyl) amino-6-nitrobenzene (HC Violet No. 1), 2- (2-

hydroxyethyl) amino-5- (bis (2-hydroxyethyl)) amino-1-nitro-benzene (HC Blue No. 2), 1- (2-hydroxyethyl) amino-2-nitro-4-N-ethyl- N-(2-hydroxyethyl) amino-benzene (HC Blue No. 12), 4-amino-3,5-dinitro- benzoic acid, 4-amino-2-nitrodiphenylamin-2'-carbonic acid, 2- (4'-amino-2'-nitroanilino)-benzoic acid, 6-nitro-2, 5-diaminopyridine, 2-amino-6-chloro- 4-nitrophenol, 4-amino-4'-nitrostilben-2, 2'-disulfonic acid, 4'-amino-4- nitrodiphenylamin-2-sulfonic acid, 4'-amino-3'-nitrobenzophenon-2- carbonic acid, 1-amino-4-nitro-2- (2'-nitrobenzylidenamino)-benzene, 2- [2- (diethylamino) ethylamino]-5-nitroaniline, 3-amino-4-hydroxy-5- nitrobenzolsulfonic acid, 3-amino-3'-nitrobiphenyl, 3-amino-4-nitro- acenaphthen, 2-amino-1-nitronaphthaline, 5-amino-6-nitrobenzo-1, 3-dioxol, 2-amino-6-nitrobenzothiazol, 4- (3-hydroxypropyl) amino-3-nitro-phenol (HC Red BN), 2-amino-4, 6-dinitro-phenol, 3-nitro-4- (2-hydroxyethyl)- aminophenol, 2- (2-hydroxyethyl) amino-4, 6-dinitrophenol, 2-amino-6-chlor- 4-nitrophenol, 2-chloro-6-ethylamino-4-nitro-phenol, 1-(2- hydroxyethyl) amino-4-methyl-2-nitrobenzene, 1-(2'-ureidoethyl) amino-4- nitrobenzene, 4-amino-2-nitro-diphenylamin-2'-carbonic acid, 6-nitro-1,2, 3,4- tetrahydrochinoxaline and 4-ethylamino-3-nitrobenzoic acid.

Suitable anthraquinone dyes suitable for the method of the present invention are the following compounds:1-[(3-aminopropyl) amino]-anthraquinone (HC Red No. 7), 2-[(2-aminoethyl) amino]-anthraquinone (HC Orange No. 5), 1,4, 5,8-tetraamino-anthrachinone (Disperse Blue 1), 1-[(2-Hydroxyethyl) amino]-4-methylamino-anthraquinone (Disperse Blue 3), 1,4-[(2-hydroxyethyl) amino] -5,8-dihydroxy- anthraquinone (Disperse Blue 7), 1,4-diamino-2-methoxy- anthraquinone (Disperse Red 11), 1-amino-4- hydroxy- anthraquinone (Disperse Red 15), 1,4-diamino-anthraquinone (Disperse Violet 1), 1-amino-4-methylamino-anthrachinone (Disperse Violet 4) and 1-amino-4-isopropylamino-anthraquinone (Disperse Violet 15).

Suitable azo dyes are for example the following compounds:
4-amino-4'-[bis (2-hydroxyethyl)] amino-azobenzene (Disperse Black 9), 4-amino-4'-nitro-azobenzene (Disperse Orange 3), 3-hydroxy-4-[(2-hydroxy-naphth-1-yl) azo)-7-nitro-naphthalin-1- sulfonic acid-chromcomplex (Acid Black 52), 1-amino-2- (3'-nitro- phenylazo)-7-phenylazo-8-naphthol-3, 6-disulfonic acid (Acid blue Nr. 29), 1-amino-2- (2'-hydroxy-4'-nitrophenylazo)-8-naphthol-3, 6-disulfonic acid (Palatinchrome green), 1-amino-2- (3'-chlor-2'-hydroxy-5'-nitrophenylazo)-8-naphthol-3, 6-disulfonic acid (Gallion) and diamino-3', 5'-dinitro-2'- hydroxy-5-methyl-azobenzene (Mordant brown 4).

Suitable cationic dyes are the following compounds: N-[4-[[4-(diethylamino) phenyl] [4-(ethylamino)-naphth-1-yl] methylen]-2,5- cyclohexadien-1-yliden]-N-ethyl-ethaniminium-chloride (Basic Blue No. 7), N- {4- [(4- (dimethylamino) phenyl) 4- (phenylamino)-1-naphthalenyl]methylen}-2, 5-cyclohexadien-1-ylidene]-N-methyl- methaniminiumchloride (Basic Blue 26), 4- [(4-aminophenyl) (4-imino-2,5- cyclohexadien-1-yliden) methyl]-2-methyl-anilin-hydrochloride (Basic Violet 14), N-{3-[(4, 5-dihydro-3-methyl-5-oxo-1-phenyl-1 H-pyrazol-4-yl) azo] phenyl}-N, N, N-trimethylammoniumchloride (Basic Yellow 57), N- [7- hydroxy-8-[(2-methoxyphenyl) azo]-naphth-2-yl]-N, N, N- trimethylammonium-chloride (Basic Red 76), N-[4-[[4- (dimethylamino) phenyl] [4-(phenylamino)-naphth-1-yl]-methylen]-2, 5- cyclohexadien-1-yliden]-N-methyl-2-methaniminiumchloride (Basic Blue 99), [8-[(4'-amino-2'-nitrophenyl) azo]-7-hydroxy-naphth-2-yl]- trimethylammoniumchloride (Basic Brown 16), [8-((4'-amino-3'-nitrophenyl) azo)-7-hydroxy-naphth-2-yl]-trimethylammoniumchloride (BasicBrown 17), Basic Yellow 87, Basic Red 51 or Basic Orange 31.

Most preference is given to a method wherein the fiber is treated with at least one sulfide dye selected from the dyes of formula

(7) $D^{+}\text{-}Z_4\text{-}M\text{-}(Z_1)_r\text{-}Y_1\text{-}S\text{-}Z_3\text{-}\left[Y_2\text{-}(Z_2)_q\text{-}M\text{-}Z_5\text{-}D^{+}\right]_n$; and

(8) $T\text{-}Z_4\text{-}Q^{+}\text{-}(Z_1)_r\text{-}Y_1\text{-}S\text{-}Z_3\text{-}\left[Y_2\text{-}(Z_2)q\text{-}Q^{+}\text{-}Z_5\text{-}T\right]_n$; wherein

Z_4 and Z_5 independently from each other are a bivalent radical selected from -N=N-; $-CR_6$=N-; $-N=CR_7$-; $-NR_8$-N=CR_9-; and $-R_{10}$C=N-NR_{11}-; wherein

R_6, R_7, R_8, R_9, R_{10} and R_{11} independently from each other are hydrogen; unsubstituted or substituted C_1-C_{14}alkyl; C_2-C_{14}alkenyl; C_5-C_{10}aryl; C_1 C_{10}alkyl-C_5-C_{10}aryl; or C_5-C_{10}aryl-C_1-C_{10}alkyl; and

D^{+} is a cationic radical of a substituted or unsubstituted aromatic or heterocyclic compound, wherein the cationic charge may be part of the aromatic compounds or part of the substituent;

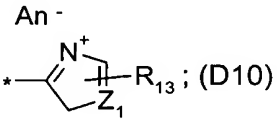
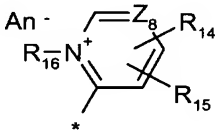
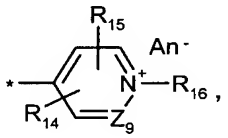
M is a bivalent radical of an aromatic or heteroaromatic substituted or unsubstituted compound;

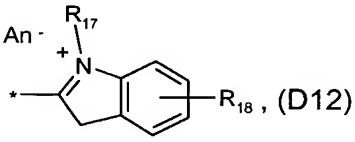
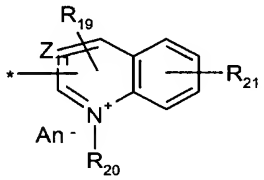
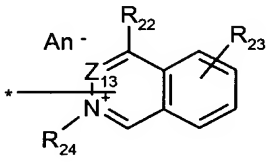
T is a radical of an aromatic substituted or unsubstituted compound;

Q^+ is a cationic biradical of a substituted or unsubstituted aromnatic or heteroaromatic compound; and

Z_1, Z_2, Z_3, Y_1, Y_2, n, r and q are defined as in formula (1).

Especially preferred is a method, wherein D is a radical of a cationic aromatic substituted or unsubstituted heterocyclic compound of formulae

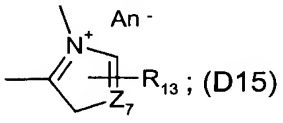
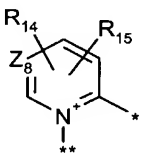
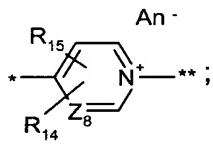
(D9)  ; (D10)  , (D10')  ,

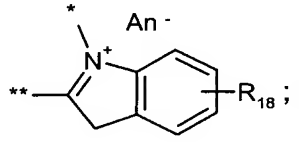
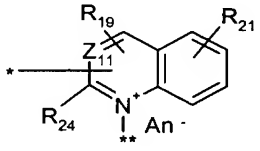
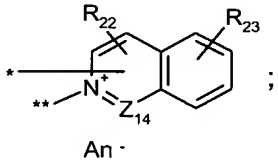
(D11)  , (D12)  or (D13) 

wherein

the asterix * indicates the bond to Z_4 and/or Z_5 of formula (7); and

Q^+ is a cationic bivalent radical of an aromatic heterocyclic compound of formulae

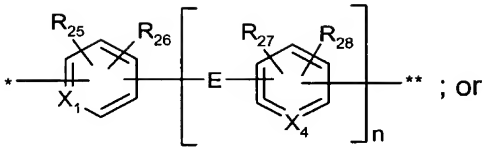
(D14)  ; (D15)  ; (D15') 

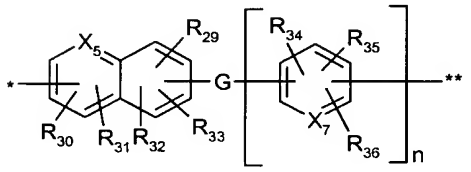
(D16)  ; (D17)  ; or (D18)  ;

wherein

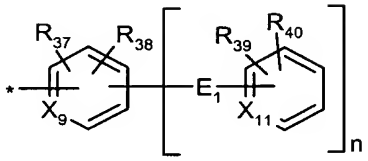
the asterix * indicates a bond to Z_4 and/or Z_5 of formula (8);

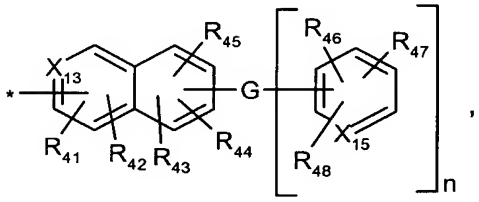
the asterix ** is a bond to Z_1 and/or Z_2 of formula (8); and

M is a bivalent radical of formulae (D19)  ; or

(D20)  , wherein

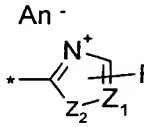
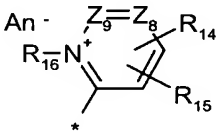
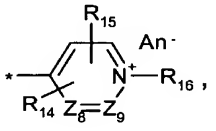
the asterix * indicates the bond to Z_4 or/and Z_5 of formula (7);
the asterix ** indicates the bond to Z_1 and/or Z_2 of formula (7); and

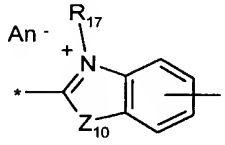
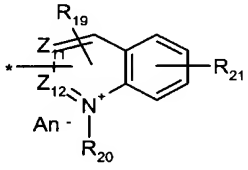
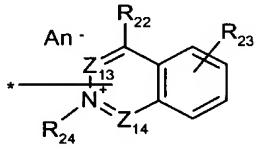
T is a radical of the compounds of formulae (D21)  ; or

(D22)  ,

The heteroaromatic cycles of the radicals of the formulae (D9) – (D22) may be interrupted by one or more than one –O-, -S-, -(SO_2)-, -C_1-C_{10}alkylene or -(NR_{52})-;

Very specially preferred is a method, wherein D^+ is a radical of a cationic aromatic substituted or unsubstituted heterocyclic compound of formulae

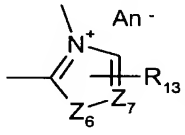
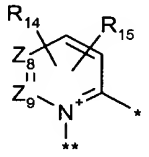
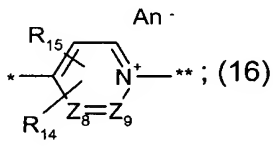
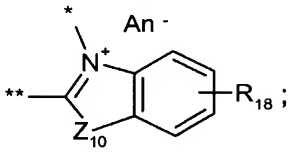
((9)  ; (10)  , (10')  ,

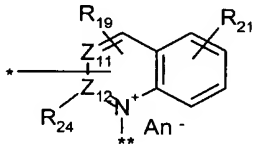
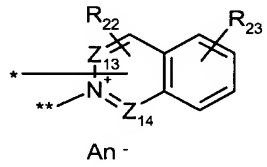
(11)  , (12)  or (13) 

wherein

the asterix * indicates the bond to Z_4 and/or Z_5 of formula (7); and

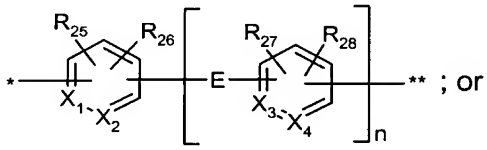
Q^+ is a cationic bivalent radical of an aromatic heterocyclic compound of formulae

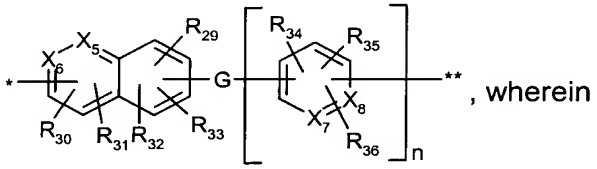
(14)  ; (15)  ; (15')  ; (16)  ;

(17)  ; or (18)  ; wherein

the asterix * indicates a bond to Z_4 and/or Z_5 of formula (8);

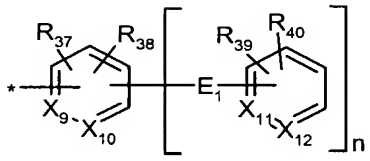
the asterix ** is a bond to Z_1 and/or Z_2 of formula (8); and

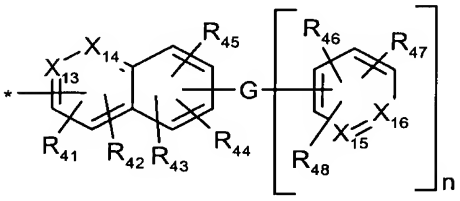
M is a bivalent radical of formulae (19)  ; or

(20)  , wherein

the asterix * indicates the bond to Z_4 or/and Z_5 of formula (7);

the asterix ** indicates the bond to Z_1 and/or Z_2 of formula (7); and

T is a radical of the compounds of formulae (21)  ; or

(22)  , wherein

the asterix * indicates the bond to Z_4 and/or Z_5 of compound of formula (8).

In the formulae (D9) – (D22) and (9) – (22)

X_1, X_2, X_3, X_4, X_5, X_6, X_7, X_8, X_9, X_{10}, X_{11}, X_{12}, X_{13}, X_{14}, X_{15} and X_{16} are independently from each other N or a radical of CR_{49},

Z_6 is –O-; –S-; or a radical of NR_{50},

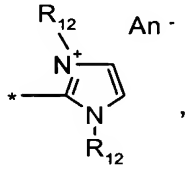
Z_7, Z_8, Z_9, Z_{10}, Z_{11}, Z_{12}, Z_{13} and Z_{14} are independently from each other N or a radical of CR_{51};

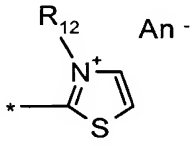
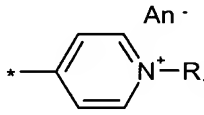
E, E_1, G and G_1 are independently from each other –O-, -S-, -(SO_2)-, -C_1-C_{10}alkylene or -(NR_{52})-;

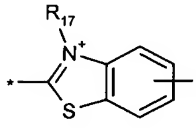
R_{13}, R_{14}, R_{15}, R_{18}, R_{19}, R_{21}, R_{22}, R_{23}, R_{25}, R_{26}, R_{27}, R_{28}, R_{29}, R_{30}, R_{31}, R_{32}, R_{33}, R_{34}, R_{35}, R_{36}, R_{37}, R_{38}, R_{39}, R_{40}, R_{41}, R_{42}, R_{43}, R_{44}, R_{45}, R_{46}, R_{47}, R_{48}, R_{49} and R_{51} are independently from each other hydrogen; halogen; C_1-C_{14}alkyl, which is saturated or unsaturated, linear or branched, substituted or unsubstituted, or interrupted or uninterrupted with heteroatoms; a radical of phenyl, which substituted or unsubstituted; a of carboxylic acid radical; sulfonic acid radical; hydroxy; nitrile; C_1-C_{16}alkoxy, (poly)-hydroxy-C_2-C_4-alkoxy; halogen; sulfonylamino; SR_{60}, NHR_{53}; $NR_{54}R_{55}$; OR_{61}; SO_2; $COOR_{62}$; $NR_{56}COR_{58}$; or $CONR_{57}$; and

R_{12}, R_{16}, R_{17}, R_{20}, R_{24}, R_{50}, R_{52}, R_{53}, R_{54}, R_{55}, R_{56}, R_{57}, R_{58}, R_{60}, R_{61} and R_{62} are each independently of the other hydrogen; unsubstituted or substituted C_1-C_{14}alkyl, C_2-C_{14}alkenyl, C_5-C_{10}aryl, C_5-C_{10}aryl-(C_1-C_{10}alkyl), or -C_1-C_{10}alkyl(C_5-C_{10}aryl); and

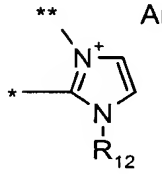
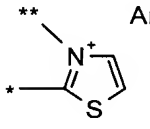
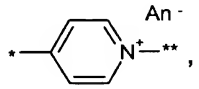
An is an anion.

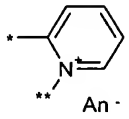
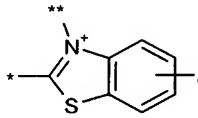
Very especially most preferred is a method, wherein D^+ is a radical of a cationic aromatic substituted or unsubstituted heterocyclic compound of formulae (23)  ,

(24)  , (25)  , (26)  or

(27)  ; wherein

* is a bond to Z_4 and/or Z_5 of formula (7); and

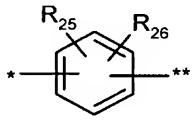
Q^+ is a biradical of a cationic aromatic substituted or unsubstituted heterocyclic compound of formulae (28)  , (29)  , (30)  ,

(31)  or (32)  ; wherein

* is a bond to Z_4 and/or Z_5 of formula (8);

** is a bond to and Z_1 and/or Z_2 of formula (8); and

M is a bivalent radical of formula

(33)  , wherein

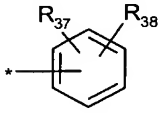
* is a bond to Z_4 and/or Z_5 of formula (7) or (8),

** is a bond to and Z_1 and/or Z_2 of formula (7) or (8); and

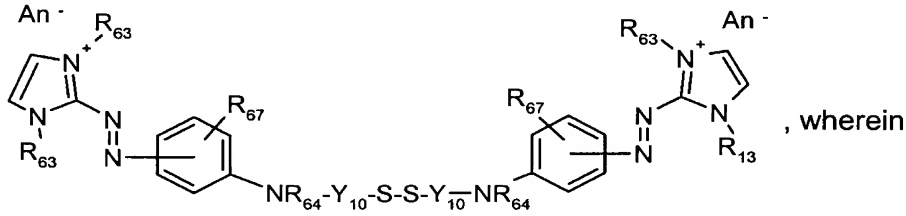
n is 1 or 0;

and

T is a radical of formulae

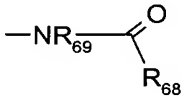
(34)  , wherein

R_{12}, R_{16}, R_{17}, R_{18}, R_{25}, R_{26}, R_{37}, R_{38} and An are defined as in claim 14.

Furthermore, very especially most preferred is a method, comprising disulfide dyes of formulae (35)  , wherein

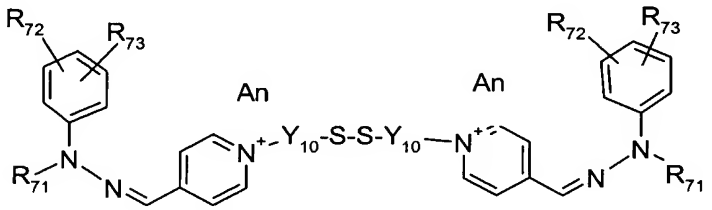
R_{63} is hydrogen; unsubstituted or substituted C_1-C_{14}alkyl; C_5-C_{10}cycloalkyl; C_2-C_{14}alkenyl; C_5-C_{10}aryl-(C_1-C_{10}alkyl); C_1-C_{10}alkyl-(C_5-C_{10}aryl); C_5-C_{10}aryl; and

R_{64} is hydrogen; ~~or~~ unsubstituted or substituted, straight-chain or branched, interrupted or uninterrubted C_1-C_{14}alkyl, C_5-C_{10}cycloalkyl, C_5-C_{10}aryl, or C_5-C_{10}aryl-(C_1-C_{10}alkyl); C_1-C_{10}alkyl(C_5-C_{10}aryl);

R_{67} is hydrogen; or a radical of formula (35a)  ;

Y_{10} is unsubstituted or substituted, straight-chain or branched, monocyclic, from C_3-alkyl upwards, or polycyclic, from C_5-alkyl upwards, interrupted or uninterrupted, C_1-C_{10}alkylene; C_5-C_{10}arylene-(C_1-C_{10}alkylene); C_1-C_{10}alkylene-(C_5-C_{10}arylene); or –C_5-C_{10}arylene; and

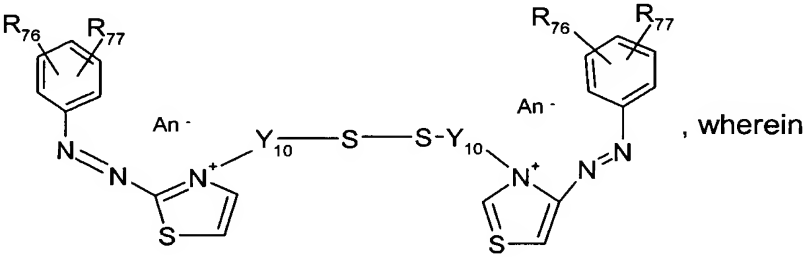
R_{68} and R_{69} are each independently of the other hydrogen, unsubstituted or substituted C_1-C_{14}alkyl, C_2-C_{14}alkenyl, -C_5-C_{10}arylen-(C_1-C_{10}alkyl), -C_1-C_{10}alkylen(C_5-C_{10}aryl), C_5-C_{10}aryl,

(36)  , wherein

R_{71} is hydrogen; unsubstituted or substituted C_1-C_{14}alkyl; C_5-C_{10}cycloalkyl; C_2-C_{14}alkenyl; C_5-C_{10}aryl; C_1-C_{10}alkyl-(C_5-C_{10}aryl); C_5-C_{10}aryl-(C_1-C_{10}alkyl);

R_{72} and R_{73} are each independently of the other hydrogen; C_1-C_{14}alkyl; C_2-C_{14}alkenyl; a radical of acarboxylic; a radical of a sulfonic acid; C_5-C_{10}aryl, hydroxy, nitril, C_1-C_{16}alkoxy, (poly)-hydroxy-C_2-C_4-alkoxy, carboxylic acid;; halogen; sulfonylamino; SR_{60}; NHR_{53}; $NR_{54}R_{55}$; OR_{61}; $COOR_{62}$; $NR_{56}COR_{58}$; or $CONR_{57}$;

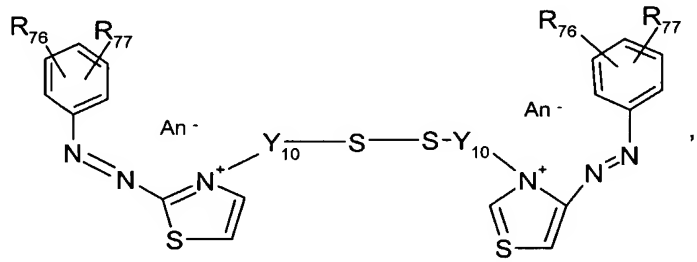
R_{53}, R_{54}, R_{55}, R_{56}, R_{57}, R_{58}, R_{60}, R_{61} and R_{62} are each independently of the other hydrogen; unsubstituted or substituted C_1-C_{14}alkyl; C_2-C_{14}alkenyl; -C_5-C_{10}arylen-(C_1-C_{10}alkyl); -C_1-C_{10}alkylene(C_5-C_{10}aryl); orC_5-C_{10}aryl;

(37)  , wherein

R_{76} and R_{77} are each independently of the other hydrogen, C_1-C_{14}alkyl, which is saturated or unsaturated, linear or branched, substituted or unsubstituted, or interrupted or

uninterrupted with heteroatoms; a radical of phenyl, which substituted or unsubstituted; a radical of carboxylic acid; C_5-C_{10}aryl, a radical of hydroxy, nitril, C_1-C_{16}alkoxy, (poly)-hydroxy-C_2-C_4-alkoxy, carboxylic acid, sulfonic acid; halogen, sulfonylamino, SR_{60}, NHR_{53} or $NR_{54}R_{55}$, OR_{61}, SO_2, $COOR_{62}$, $NR_{56}COR_{58}$, $CONR_{57}$;

R_{53}, R_{54}, R_{55}, R_{56}, R_{57}, R_{58}, R_{60}, R_{61} and R_{62} are each independently of the other hydrogen, unsubstituted or substituted C_1-C_{14}alkyl, C_2-C_{14}alkenyl, -C_5-C_{10}arylen-(C_1-C_{10}alkyl), -C_1-C_{10}alkylen(C_5-C_{10}aryl), C_5-C_{10}aryl,

(38)  , wherein

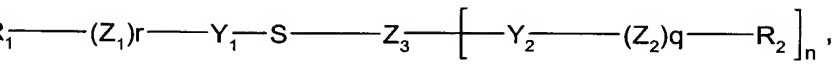
R_{79}, R_{78} and R_{80} are each independently of the other hydrogen; C_1-C_{14}alkyl, which is saturated or unsaturated, linear or branched, substituted or unsubstituted, or interrupted or uninterrupted with heteroatoms; a radical of phenyl, which substituted or unsubstituted; a radical of carboxylic acid; C_5-C_{10}aryl, a radical of hydroxy, nitril, C_1-C_{16}alkoxy, (poly)-hydroxy-C_2-C_4-alkoxy; carboxylic acid; sulfonic acid; halogen; sulfonylamino; SR_{60}; NHR_{53}; $NR_{54}R_{55}$; OR_{61}; SO_2; $COOR_{62}$; $NR_{56}COR_{58}$; or $CONR_{57}$;

R_{53}, R_{54}, R_{55}, R_{56}, R_{57}, R_{58}, R_{60}, R_{61} and R_{62} are each independently of the other hydrogen; unsubstituted or substituted C_1-C_{14}alkyl; C_2-C_{14}alkenyl; C_5-C_{10}arylene-(C_1-C_{10}alkyl), C_1-C_{10}alkylene(C_5-C_{10}aryl), C_5-C_{10}aryl,

More preferred are:

- compounds o formula (35), wherein R_{63} is methyl;
- compounds of formula (36), wherein R_{72} is hydrogen; and R_{72} is in the para-postion of the phenyl moiety;
- compounds of formula (37), wherein R_{76} is hydrogen; and R_{77} is in the para-postion of the phenyl moiety;
- compounds of formula (38), wherein R_{78} is hydrogen; and R_{79} is in the para-postion of the phenyl moiety.

The compounds of formula

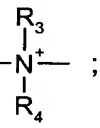
(1')  , wherein

R_1 and R_2 each independently from each other are a residue of an organic dye;

Y_1 and Y_2 independently from each other are C_1-C_{10}alkylene;

Z_1 and Z_2 independently from each other are –C(O)-; -C_2-C_{12}alkenylene-; -$(CH_2CH_2-O)_{1-5}$-;

C_1-C_{10}alkylene(C_5-C_{10}arylene); C_5-C_{10}arylene; C_5-C_{10}cycloalkylene, -C(O)O-, -OCO-;

-N(R_3)-;  ; -CON(R_4)-; -(R_5)NC(O)-; –O- -S-; -S(O)-; or –$S(O)_2$-;

R_3, R_4 and R_5 are each independently from each other hydrogen; C_1-C_{14}alkyl; C_2-C_{14}alkenyl;

C_6-C_{10}aryl; C_1-C_5alkyl-C_5-C_{10}aryl; or-C_5-$C_{10}C_5$-C_{10}aryl;

r, q and n independently from each other are 0; or 1,

if n is 0,

Z_3 is hydrogen; and

if n is 1,

Z_3 is –S-;

Are novel and represent another subject of the present inventio.

The present invention also relates to the novel compounds of formulae (35), (36), (37) and (38).

Alkylene is generally C_1-C_{10}alkylene, for example methylene, ethylene, propylene, isopropylene, n-butylene, sec-butylene, tert-butylene, n-pentylene, 2-pentylene 3-pentylene, 2,2'-dimethylpropylene, cyclopentylene, cyclohexylene, n-hexylene, n-octylene, 1,1',3,3'-tetramethylbutylene, 2-ethylhexylene, nonylene or decylene.

Alkylene may be straight-chain, branched, or, from C_5alkyl upwards, monocyclic or polycyclic, and may be interrupted by hetero atoms, such as such as O, S, -CO-, N, NH, NR_{54}, -OCO-, -CO(OR_4)-, -CONR_4-, -(R_5)NC(O)-; for example C_1-C_{10}alkylene may be a resisue such as: –CH_2CH_2-O-CH_2CH_2-O-CH_2CH_2-, or -CH_2CH_2-O-CH_2CH_2-, -CH_2CH_2-O-CH_2-, -CH_2-O-CH_2-, –CH_2CH_2-CH_2CH_2-O-CH_2-CH_2-, -CH_2CH_2-CH($N(CH_3)_2$)-CH_2-CH_2-, CH_2-NH_2-CH_2-CH_2, or–CH_2CH_2-NH-CH_2CH_2-, –CH_2CH_2-NCH_3-CH_2CH_2-, or –CO-CH_2-, or -CH_2CO-, or –CH_2CH_2-NHCO-CH_2CH_2-, or –CH_2CH_2-CONH-CH_3-CH_2CH_2-, –CH_2CH_2-NCH_3CO-CH_2CH_2-,

or $-CH_2CH_2-CONCH_3-CH_3-CH_2CH_2-$, or $-CH_2-NHCO-CH_2CH_2-$, or $-CH_2CH_2-NHCO-CH_2-$, or $-CH_2CH_2-CONH-CH_2-$ or $-CH_2-CONH-CH_2CH_2-$.

Arylene is generally C_6-C_{10}arylene; for example phenyl or naphthyl;

Aryl-alkylene is for example C_5-C_{10}aryl-C_1-C_{10}alkylene, C_6-C_{10}aryl-C_1-C_2alkylene, alkyl-arylene is for example C_1-C_{10}alkyl-C_5-C_{10}arylene or C_1-C_2alkyl-C_6-C_{10}arylene.

C_5-C_{10}cycloalkylene is for example cyclopentylene, cyclohexylene, morpholylene or piperidinylene.

In the present invention subsituents may be chosen from the following groups: hydroxyl, C_1-C_{16}alkyl, C_5-C_{10}aryl, C_1-C_{16}alkoxy, - COOH, sulfonic acid, sulfonylamino, $-SR_{60}$, -OCO-, $-COOR_4$, $-CONR_4$, $-(R_5)NC(O)$, - S(O)-, $-SO_2$, cyanide, nitrile, halide, aryl, aralkyl, alkylaryl and $NR_{54}R_{55}$, wherein
R_4, R_5, R_{54}, R_{55} and R_{60} have the same defintion and preferences as given above.

C_1-C_{16}alkyl is for example, methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, n-pentyl, 2-pentyl, 3-pentyl, 2,2'-dimethylpropyl, cyclopentyl, cyclohexyl, n-hexyl, n-octyl, 1,1',3,3'-tetramethylbutyl or 2-ethylhexyl, nonyl, decyl, undecy, dodecyl, tredecyl, tetradecyl, pentadecyl or haxadecly.

C_1-C_6alkoxy is O–C_1-C_6alkyl, preferably O–C_1-C_4alkyl.

C_5-C_{10}aryl-C_1-C_{10}alkylene is, for example, phenyl-C_1-C_{10}alkylene or naphthyl-C_1-C_{10}alkylene.

C_6-C_{10}aryl-C_1-C_2alkylene and C_1-C_2alkyl-C_6-C_{10}arylene are, for example, phenyl-C_1-C_{10}alkylene or naphthyl-C_1-C_{10}alkylen.

Halide is, for example, fluoride, chloride, bromide or iodide, especially chloride and fluoride.

"Anion" denotes, for example, an organic or inorganic anion, such as halide, preferably chloride and fluoride, sulfate, hydrogen sulfate, phosphate, boron tetrafluoride, carbonate, bicarbonate, oxalate or C_1-C_8alkyl sulfate, especially methyl sulfate or ethyl sulfate; anion

also denotes lactate, formate, acetate, propionate or a complex anion, such as the zinc chloride double salt.

The anion is especially a halide, preferably chloride or fluoride, sulfate, hydrogen sulfate, methyl sulfate, ethyl sulfate, phosphate, formate, acetate or lactate.
The anion is more especially fluoride, chloride, methyl sulfate, ethyl sulfate, formate or acetate.

In the present invention protein disulfidisomerase (EC 5.3.4.1) is an enzyme of the enzym category EC 5.3.4.1. These enzymes preferably catalyse the ismerisation of intermolecular and intramolecular disulfid-bonds in proteinis. The EC (Enzyme commission) number is provided from the " Nomenclature Committee of the International Uniion of Biochemistry and Molecular Biology" (IUBMB). A complete list of the characertized enzymes of the enzymens categories according to IUBMB is provided by data base of SwissProt under http://www.expasy.ch.

In the present invention the residue of an organic dye is substituted or unsubstituted.

In the present invention biradical or radical of a heterocyclic compound is for example a biradical or radical of thiophenyl, 1,3-thiazolyl, 1,2-thiazolyl, 1,3-benzothiazolyl, 2,3-benzothiazolyl, imidazolyl, 1,3,4-thiadiazolyl, 1,3,5-thiadiazolyl, 1,3,4-triazolyl, pyrazolyl, benzimidazolyl, benzopyrazolyl, pyridinyl, quinolinyl, pyrimidinyl and isoxazolyl.

Preferred biradical or radical of a heterocyclic compound is for example 1,3-thiazolyl, 1,2-thiazolyl, 1,3-benzothiazolyl, 2,3-benzothiazolyl, imidazolyl, 1,3,4-thiadiazolyl, 1,3,5-thiadiazolyl, 1,3,4-triazolyl, pyrazolyl, benzimidazolyl, benzopyrazolyl, pyridinyl, quinolinyl, pyrimidinyl and isoxazolyl. More preferred cationic heterocyclic compounds are imidazolyl, pyridinyl, 1,3,4-triazolyl and 1,3-thiazolyl.

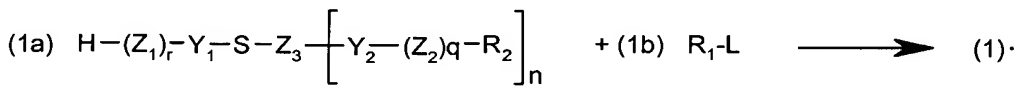
In the present invention a biradical or radical of an aromatic compound is for example phenyl, naphthyl, thiophenyl, 1,3-thiazolyl, 1,2-thiazolyl, 1,3-benzothiazolyl, 2,3-benzothiazolyl, imidazolyl, 1,3,4-thiadiazolyl, 1,3,5-thiadiazolyl, 1,3,4-triazolyl, pyrazolyl, benzimidazolyl, benzopyrazolyl, pyridinyl, quinolinyl, pyrimidinyl and isoxazolyl, aminodiphenyl, aminodiphenylether or azobenzenyl.

The biradical or radical of a heterocyclic or aromatic compound is unsubstituted or mono- or poly-substituted, for example by C_1-C_4alkyl, C_1-C_4alkoxy, C_1-C_4alkylthio, halogen, e.g. fluorine, bromine or chlorine, nitro, trifluoromethyl, CN, SCN, C_1-C_4alkylsulfonyl, phenylsulfonyl, benzylsulfonyl, di-C_1-C_4alkylaminosulfonyl, C_1-C_4alkyl-carbonylamino, C_1-C_4alkoxysulfonyl or by di-(hydroxy-C_1-C_4alkyl)-aminosulfonyl.

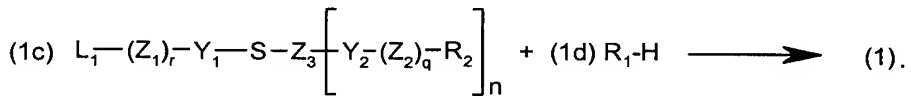
A further emodiment of the present inveintion relates to processes for the preparation of the dyes of formula (1).

Generally, the process comprises a nucleophilic substitution of an organic compound by a sulfide and/or disulfide derivative containing at least one nucleophil group, or a electrophilic substitution of an organic compound by a sulfid and/or disulfid derivative containing at least one electrophilic groups.

A preferred process for the preparation comprises reacting a compound of formula (1a) with the compound of formula (1b) according to the following reaction scheme:



A further preferred process for the preparation of compounds of formula (1) comprises reacting a compound of formula (1c) with the compound of formula (1d) according to the following reaction scheme:



In the formula (1a), (1b), (1c) and (1d)
L_1 is a leaving group; and
R_1, R_2, Z_1, Z_2, Z_3, Y_1, Y_2, r, q and n are defined as in formula (1).

The reaction is generally initiated by contacting; for example by mixing together the starting compounds or by dropwise addition of one starting compound to the other.

Customary, the temperature is in the range of 273 to 300 K, preferably is in the range of 290 to 300 K during the mixing of the starting compounds.

The reaction time is generally dependent on the reactivity of the starting compounds, on the reaction temperature chosen and on the desired conversion. The chosen duration of reaction is usually in the range from one hour to three days.

The reaction temperature for the reaction of the compounds is advisable to select in the range from 273 to 340K, especially in the range from 273 to 335K.

The reaction pressure chosen is generally in the range from 70 kPa to 10 MPa, especially from 90 kPa to 5 MPa, and is more especially atmospheric pressure.

It may by desirable to conduct the reaction of compounds in the presence of a catalyst.

The molar ratio of compound of formula (1a) to the catalyst is generally selected in the range from 10:1 to 1:5, especially in the range from 10:1 to 1:1.

Suitable catalysts are for example an alkali metal C_1-C_6alkyloxide, such as sodium-, potassium or lithium C_1-C_6alkyloxide, preferably sodium methoxide, potassium methoxide or lithium methoxide, or sodium ethoxide, potassium ethoxide or lithium ethoxide; or tertiary amines, for example, such as chinuclidine, N-methylpiperidine, pyridine, trimethylamine, triethylamine, trioctylamine, 1,4-diazabicyclo[2.2.2]octan, chinuclidine, N-methylpiperidine; or alkalimetal acetate, for example such as sodium acetate, potassium acetate, or lithium acetate.
Preferred are potassium acetate, sodium methoxide, pyridine and 1,4-diaza-bicyclo[2.2.2]octan.

In addition, the reaction may be carried out with or without a solvent, but is preferably carried out in the presence of a solvent, preferably organic solvents or solvent mixtures.

Solvents are organic solvents and water, or a mixture of organic solvents or a mixture of organic solvents and water.

Organic solvents are for example, protic or aprotic polar organic solvents, such as alcohols, for example methanol, ethanol, n-propanol, isopropanol, butanol or glycols, especially isopropanol, or nitrile, such as acetonitrile or propionitrile, or amide, such as dimethyl-formamide, dimethylacetamide or N-methylpyridine, N-methylpyrolidon, or sulfoxide, such as dimethylsulfoxide, or mixtures thereof.

The product prepared according to the process of the present invention may be advantageously worked up and isolated, and if desired be purified.

Customary, the work up starts by decreasing the temperature of the reaction mixture in the range from 280 to 300 K, especially in the range from 290 to 300 K.

It may be of advantageous to decrease the temperature slowly, over a period of several hours.

In general, the reaction product is usually filtered and then washed with water or a salt solution and subsequently dried.

Filtration is normally carried out in standard filtering equipment, for example Büchner funnels, filter presses, pressurised suction filters, preferably *in vacuo*.

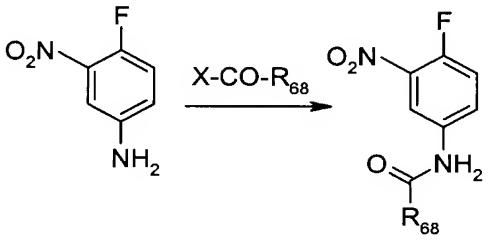
The temperature for the drying is dependent on the pressure applied. Drying is usually carried out *in vacuo* at 50-200 mbar.

The drying is usually carried out at a temperature in the range from 313 to 363 K, especially from 323 to 353 K, and more especially in the range from 328 to 348 K.

Advantageously the product is purified by recrystallisation after isolation.

Organic solvents and solvent mixtures are suitable for the recrystallisation, preferably alcohols, for example methanol, ethanol, 2-propanol or butanol, especially 2-propanol.

The present invention also relates to a process for the preparation of compounds of formula

(70)  , which comprises

a. acylating of 4-fluoro-3-nitroaniline with an acylating agent as shown in the above formula

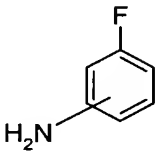
b. hen reducing the nitro group to the amino group,

c. then diazotizing the acylated 4-Fluoro-3-amino-aniline, and

d. then coupling the diazotized with imidazole, and

e. then alkylating the intermediate compound with an alkylating agent; or

a_1) diazotizing and coupling of a compound of formula, and then

b_1) alkylating the intermediate compound with an alkylating agent  ; wherein

R_{68} is hydrogen, unsubstituted or substituted C_1-C_{14}alkyl, C_2-C_{14}alkenyl, -C_5-C_{10}arylen-(C_1-C_{10}alkyl), -C_1-C_{10}alkylen(C_5-C_{10}aryl), C_5-C_{10}aryl,

The acylation, reduction, diazotation, coupling and alkylation can be conducted by methods known per se.

The dyes of formula (1) according to the invention are suitable for dyeing organic materials, such as keratin-containing fibers, wool, leather, silk, cellulose or polyamides, cotton or nylon, and preferably human hair. The dyeings obtained are distinguished by their depth of shade and their good fastness properties to washing, such as, for example, fastness to light, sham-pooing and rubbing. The stability, in particular the storage stability of the dyes according to the invention are excellent.

Gernerally, hair dyeing agents on a synthetic base may be classiefied itnto three groups:

- temporary dyeing agents
- semipermanent dyeing agents, and

- permanent dyeing agents.

The multiplicity of shades of the dyes can be increased by combination with other dyes.

Therefore the dyes of formula (1) of the present invention may be combined with dyes of the same or other classes of dyes, especially with direct dyes, oxidation dyes; dye precursor combinations of a coupler compound as well as a diazotized compound, or a capped diazotized compound; and/or cationic reactive dyes.

Direct dyes are of natural origin or may be prepared synthetically. They are uncharged, cationic or anionic, such as acid dyes.

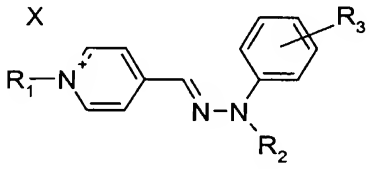
The dyes of formula (1) may be used in combination with at least one single direct dye different from the dyes of formula (1).
Direct dyes do not require any addition of an oxidizing agent to develop their dyeing effect. Accordingly the dyeing results are less permanent than those obtained with permanent dyeing compositions. Direct dyes are therefore preferably used for semipermanent hair dyeings.

Examples of direct dyes are described in "Dermatology", edited by Ch. Culnan, H. Maibach, Verlag Marcel Dekker Inc., New York, Basle, 1986, Vol. 7, Ch. Zviak, The Science of Hair Care, chapter 7, p. 248-250, and in "Europäisches Inventar der Kosmetikrohstoffe", 1996, published by The European Commission, obtainable in diskette form from the Bundesverband der deutschen Industrie- und Handelsunternehmen für Arzneimittel, Reformwaren und Körperpflegemittel e.V., Mannheim.

More preferred direct dyes which are useful for the combination with at least one single dye of formula (1), especially for semi permanent dyeing, are: 2-amino-3-nitrophenol, 2-amino-4-hydroxyethylamino-anisole sulfate, 2-amino-6-chloro-4-nitrophenol, 2-chloro-5-nitro-N-hydroxyethylene-p-phenylendiamine, 2-hydroxyethyl-picramic acid, 2,6-diamino-3-((pyridine-3yl)-azo)pyridine, 2-nitro-5-glyceryl-methylanil., 3-methylamino-4-nitro-phenoxyethanol, 4-amino-2-nitrodiphenyleneamine-2'-carboxilic acid, 6-nitro-1,2,3,4,-tetrahydroquinoxal., 4-N-ethyl-1,4-bis(2'-hydroxyethylamino-2-nitrobenzene hydrochloride, 1-methyl-3-nitro-4-(2'-hydroxyethyl)-aminobenzene, 3-nitro-p-hydroxyethyl-aminophenol, 4-amino-3-nitrophenol, 4-

hydroxypropylamine-3-nitrophenol, hydroxyanthrylaminopropylmethyl morphlino methosulfate, 4-nitrophenyl-aminoethylurea, 6-nitro-p-toluidine, Acid Blue 62, Acid Blue 9, Acid Red 35, Acid Red 87 (Eosin), Acid Violet 43, Acid Yellow 1, Basic Blue 3, Basic Blue 6, Basic Blue 7, Basic Blue 9, Basic Blue 12, Basic Blue 26, Basic Blue 99, Basic Brown 16, Basic Brown 17, Basic Red 2, Basic Red 22, Basic Red 76, Basic Violet 14, Basic Yellow 57, Basic Yellow 9, Disperse Blue 3, Disperse Orange 3, Disperse Red 17, Disperse Violet 1, Disperse Violet 4, Disperse Black 9, Fast Green FCF, HC Blue 2, HC Blue 7, HC Blue 8, HC Blue 12, HC Orange 1, HC Orange 2, HC Red 1, HC Red 10-11, HC Red 13, HC Red 16, HC Red 3, HC Red BN, HC Red 7, HC Violet 1, HC Violet 2, HC Yellow 2, HC Yellow 5, HC Yellow 5, HC Yellow 6, HC Yellow 7, HC Yellow 9, HC Yellow 12, HC Red 8, hydroxyethyl-2-nitro-p-toluidine, N,N-Bis-(2-Hydroxyethyl)-2-nitro-p-phenylendiamine, HC Violet BS, Picramic Acid, Solvent Green 7.

Furthermore, the dyes of formula (1) may be combined with at least one cationic azo dye, for example the compounds disclosed in GB-A-2 319 776 as well as the oxazine dyes described in DE-A-299 12 327 and mixtures thereof with the other direct dyes mentioned therein, and even more preferred with cationic dyes such as Basic Yellow 87, Basic Orange 31 or Basic Red 51, or with cationic dyes as described in WO 01/66646, especially example 4, or with cationic dyes as described in WO 02/31056, especially example 6 (compound of formula 106); or the cationic dye of formula (3) as described in EP-A-714,954, or with a yellow cationic dye of formula

(DD1)  , wherein

R_1 and R_2 are each independently of the other a C_1-C_8alkyl; or an unsubstituted or substituted benzyl;

R_3 is hydrogen; C_1-C_8alkyl; C_1-C_8alkoxy; cyanide; or halide; preferably hydrogen; and

X^- is an anion; and preferably a compound of formula (DD1), wherein

R_1 is methyl; R_2 is benzyl; R_3 is hydrogen; and X^- is an anion; or wherein

R_1 is benzyl; R_2 is benzyl; R_3 is hydrogen; and X^- is an anion; or wherein

R_1 is benzyl; R_2 is methyl; R_3 is hydrogen; and X^- is an anion.

Furthermore, cationic nitroaniline and anthraquinone dyes are useful for a combination with a dye of formula (1), for example the dyes as described in the following patent specifications: US-5 298 029, especially in col 2, l. 33 to col 5, l. 38; US-5 360 930, especially in col 2, l. 38 to col 5, l. 49; US-5 169 403, especially in col 2, l. 30 to col 5, l. 38; US-5 256 823, especially in col 4, l. 23 to col 5, l. 15; US-5 135 543, especially in col 4, l. 24 to col 5, l. 16; EP-A-818 193, especially on p. 2, l. 40 to p. 3, l. 26; US-5 486 629, especially in col 2, l. 34 to col 5, l. 29; and EP-A-758 547, especially on p. 7, l. 48 to p. 8, l. 19.

The dyes of formula (1) may also be combined with acid dyes, for example the dyes which are known from the international names (Color index), or trade names.

Preferred acid dyes which are useful for the combination with a dye of formula (1) are described in US Patent 6,248,314. They include Red Color No. 120, Yellow Color No. 4, Yellow Color No. 5, Red Color No. 201, Red Color No. 227, Orange Color No. 205, Brown Color No. 201, Red Color No. 502, Red Color No. 503, Red Color No. 504, Red Color No. 506, Orange Color No. 402, Yellow Color No. 402, Yellow Color No. 406, Yellow Color No. 407, Red Color No. 213, Red Color No. 214, Red Color No. 3, Red Color No. 104, Red Color No. 105(1), Red Color No. 106, Green Color No. 2, Green Color No. 3, Orange Color No. 207, Yellow Color No. 202(1), Yellow Color No. 202(2), Blue Color No. 202, Blue Color No. 203, Blue Color No. 205, Blue Color No. 2, Yellow Color No. 203, Blue Color No. 201, Green Color No. 201, Blue Color NO. 1, Red Color No. 230(1), Red Color No. 231, Red Color No. 232, Green Color No. 204, Green Color No. 205, Red Color No. 401, Yellow Color No. 403(1), Green Color No. 401, Green Color No. 402, Black Color No. 401 and Purple Color No. 401, especially Black Color No. 401, Purple Color 401, Orange Color No. 205.

These acid dyes may be used either as single component or in any combination thereof.

Hair dye compositions comprising an acid dye are known. They are for example described in "Dermatology", edited by Ch. Culnan, H. Maibach, Verlag Marcel Dekker Inc., New York, Basle, 1986, Vol. 7, Ch. Zviak, The Science of Hair Care, chapter 7, p. 248-250, especially on p. 253 and 254.

Hair dye compositions which comprise an acid dye have a pH of 2-6, preferably 2-5, more preferably 2.5-4.0.

The dyes of formula (1) according to the present invention may also readily be used in combination with acid dyes and/or adjuvants, for example

- acid dyes and an alkylene carbonate, as described in US patent 6,248,314, especially in examples 1 and 2;
- acid hair dye compositions comprising various kinds of organic solvents represented by benzyl alcohol as a penetrant solvent have good penetrability into hair, as described in Japanese Patent Application Laid-Open Nos. 210023/1986 and 101841/1995;
- acid hair dye compositions with a water-soluble polymer or the like to prevent the drooping of the hair dye composition, as described for example in Japanese Patent Application Laid-Open Nos. 87450/1998, 255540/1997 and 245348/1996;
- acid hair dye compositions with a water-soluble polymer of aromatic alcohols, lower alkylene carbonates, or the like as described in Japanese Patent Application Laid-Open No. 53970/1998 and Japanese Patent Invention No. 23911/1973.

The dyes of formula (1) may also be combined with uncharged dyes, for example selected from the group of the nitroanilines, nitrophenylenediamines, nitroaminophenols, anthraquinones, indophenols, phenazines, phenothiazines, bispyrazolons, ~~or~~ bispyrazol aza derivatives and methines.

Furthermore, the dyes of formula (1) may also be used in combination with oxidation dye systems.

Oxidation dyes, which, in the initial state, are not dyes but dye precursors are classified according to their chemical properties into developer and coupler compounds.

Suitable oxidation dyes are described for example in

- DE 19 959 479, especially in col 2, l. 6 to col 3, l. 11;
- "Dermatology", edited by Ch. Culnan, H. Maibach, Verlag Marcel Dekker Inc., New York, Basle, 1986, Vol. 7, Ch. Zviak, The Science of Hair Care, chapter 8, on p. 264 - 267 (oxidation dyes);

Preferred developer compounds are for example primary aromatic amines, which are substituted in the para- or ortho- position with a substituted or unsubstituted hydroxy- or amino residue, or diaminopyridine derivatives, heterocyclic hydrazones, 4-aminopyrazol

derivatives, 2,4,5,6-tetraaminopyrimidine derivatives, or unsaturated aldehydes as described in DE 19 717 224, especially on p. 2, l. 50 to l. 66 and on p. 3 l. 8 to l. 12, or cationic developer compounds as described in WO 00/43367, especially on p., 2 l. 27 to p. 8, l. 24, in particular on p. 9, l. 22 to p. 11, l. 6.

Furthermore, developer compounds in their physiological compatible acid addition salt form, such as hydrochloride or sulfate can be used. Developer compounds, which have aromatic OH radicals are also suitable in their salt form together with a base, such as alkali metal-phenolates.

Preferred developer compounds are disclosed in DE 19959479, p. 2, l. 8 – 29.

More preferred developer compounds are p-phenylendiamine, p-toluylendiamine, p-, m- o-aminophenol, N,N-bis-(2-hydroxyethyl)-p-phenylenediamine sulfate, 2-amino-4-hydroxyethylaminoanisole sulfate, hydroxyethyl-3,4-methylenedioxyanil., 1-(2'-hydroxyethyl)-2,5-diaminobenzene, 2,6-dimethoxy-3,5-diamino-pyridine, hydroxypropyl-bis-(N-hydroxy-ethyl-p-phenylenediamine) hydrochloride, hydroxyethyl-p-phenylenediamine sulfate, 4-amino-3-methylphenol, 4-methylaminophenol sulfate, 2-aminomethyl-4-aminophenol, 4,5-di-amino-1-(2-hydroxyethyl)-1H- pyrazol, 4-amino-m-cresol, 6-amino-m-cresol, 5-amino-6-chloro-cresol, 2,4,5,6-tetraaminopyrimidine, 2-hydroxy-4,5,6-triaminopyrimidine or 4-hydroxy-2,5,6-triaminopyrimidine sulfate.

Preferred coupler compounds are m-phenylendiamine derivatives, naphthole, resorcine and resorcine derivatives, pyrazolone and m-aminophenol derivatives, and most preferably the coupler compounds disclosed in DE 19959479, p.1, l. 33 to p. 3, l. 11.

The dyes of formula (1) may also be used together with unsaturated aldehydes as disclosed in DE 19 717 224 (p. 2, ~~l.~~ 50 to ~~l.~~ 66 and on p. 3 ~~l.~~ 8 to ~~l.~~ 12) which may be used as direct dyes or, alternatively together with oxidation dye precursors.

Further preferred for a combination with a dye of formula (1) are the following oxidation dye precursors:

- the developer/-coupler combination 2,4,5,6-tetraaminopyrimidine and 2-methylresorcine for assessing of red shades;

- p-toluenediamine and 4-amino-2-hydroxytoluene for assessing of blue-violet shades;
- p-toluenediamine and 2-amino-4-hydroxyethylaminoanisole for assessing of blue shades;
- p-toluenediamine and 2,4-diamino-phenoxyethynol for assessing of blue shades;
- methyl-4-aminophenol and 4-amino-2-hydroxytloluene for assessing of orange shades;
- p-toluenediamine and resorcine for assessing of brown-green shades;
- p-toluenediamine and 1-naphthol for assessing of blue-violet shades, or
- p-toluenediamine and 2-methylresorcine for assessing of brown-gold shades.

Furthermore, autooxidizable compounds may be used in combination with the dyes of formula (1).

Autooxidizable compounds are aromatic compounds with more than two substituents in the aomatic ring, which have a very low redox potential and will therefore be oxidized when exposed to the air. The dyeings obtained with these compounds are very stable and resistant to schampoo.

Autooxidizable compounds are for example benzene, indol, or indol., especially 5,6-dihydroxyindol or 5,6-dihydroxyindol. derivatives as described in WO 99/20234, especially on p. 26, l. 10 to p. 28, l. 15, or in WO 00/28957 on p. 2, third paragraph.

Preferred autooxidizable benzene derivatives are 1,2,4-trihydroxybenzene, 1-methyl-2,4,5-trihydroxybenzene, 2,4-diamnio-6-methylphenol, 2-amino-4-methylaminophenol, 2,5-diamino-4-methyl-phenol, 2,6-diamino-4-diethylaminophenol, 2,6-diamino-1,4-dihydroxybenzene, and the salts of these compounds, which are accessible with acid.

Preferred autooxidizable indol derivatives are 5,6-dihydroxyindol, 2-methyl-5,6-dihydroxyindol, 3-methyl-5,6-dihydroxyindole, 1-methyl-5,6-dihydroxyindol, 2,3-dimethyl-5,6-dihydroxyindol, 5-methoxy-6-dihydroxyindol, 5-acetoxy-6-hydroixyindol, 5,6-diacetoxyindol, acid of 5,6-dihydroxyindol-2-carbonacid, and the salts of these compounds, which are accessible with acid.

The dyes of formula (1) may also be used in combination with naturally occurring dyes, such ashenna red, henna neutral, henna black, camomile blossom, sandalwood, black tea,

Rhamnus frangula bark, sage, campeche wood, madder root, catechu, sedre and alkanet root. Such dyeings are described, for example, in EP-A-404 868, especially on p. 3, l. 55 to p. 4, l. 9.

Furthermore, the dyes of formula (1) may also be used in combination with capped diazotised compounds.

Suitable diazotised compounds are for example the compounds of formulae (1) – (4) in WO 2004/019897 (bridging gages 1 and 2) and the corresponding watersoluble coupling components (I) –(IV) as disclosed in the same reference on p. 3 to

Further preferred dyes or dye combinations which are useful for the combination with a dye of formula (1) according to the present invention are described in

(DC-01): WO 95/01772, wherein mixtures of at least two cationic dyes are disclosed, especially p. 2, l. 7 to p. 4, l. 1, preferably p. 4, l. 35 to p. 8, l. 21; formulations p. 11, last § - p. 28, l. 19;

(DC-02): US 6,843,256, wherein cationic dyes are disclosed, especially the compounds of formulae (1), (2), (3) and (4) (col. 1, l. 27 – col. 3, l. 20, and preferably the compounds as prepared in the examples 1 to 4 (col. 10, l.42 to col. 13, l. 37; formulations col. 13, l. 38 to col. 15, l. 8;

(DC-03): EP 970 685, wherein direct dyes are described, especially p. 2, l. 44 to p. 9, l. 56 and preferably p. 9, l. 58 to p. 48, l. 12; processes for dyeing of keratin-containing fibers especially p. 50, l. 15 to 43; formulations p. 50, l. 46 to p. 51, l. 40;

(DC-04): DE-A-19 713 698, wherein direct dyes are described, especially p. 2, l. 61 to p. 3, l. 43; formulations p. 5, l. 26 to 60;

(DC-05): US 6,368,360, wherein directd dyes (col. 4, l. 1 to col. 6, l. 31) and oxidizing agents (col. 6, l. 37 –39) are disclosed; formulations col. 7, l. 47 to col. 9, l. 4;

(DC-06): EP 1 166 752, wherein cationic dyes (p. 3, l. 22 – p. 4, l. 15) and anionic UV-absorbers (p. 4, l. 27 – 30) are disclosed; formulations p. 7, l. 50 – p. 9, l. 56;

(DC-07): EP 998,908, wherein oxidation dyeings comprising a cationic direct dye and pyrazolo-[1,5-a]-pyrimidines (p. 2, l. 48 – p. 4, l. 1) are disclosed; dyeing formulations p. 47, l. 25 to p. 50, l. 29;

(DC-08): FR-2788432, wherein combinations of cationic dyes with Arianors are disclosed, especially p. 53, l. 1 to p. 63, l. 23, more especially p. 51 to 52, most especially Basic

Brown 17, Basic brown 16, Basic Red 76 and Basic Red 118, and/or at least one Basic Yellow 57, and/or at least one Basic Blue 99; or combinations of arianoren and/or oxidative dyes, especially p. 2, l. 16 to p. 3, l. 16; dyeing formulations on p. 53, l. 1 to p. 63, l. 23;

(DC-09): DE-A-19 713 698, wherein the combinations of direct dyes and permanent-wave fixing comprising an oxidation agent, an oxidation dye and a direct dye are disclosed; especially p. 4, l. 65 to p. 5, l. 59;

(DC-10): EP 850 638, wherein developer compounds and oxidizing agents are disclosed; especially p. 2, l. 27 to p. 7, l. 46 and preferably p. 7, l. 20 to p. 9, l. 26; dyeing formulations p. 2, l. 3-12 and l. 30 to p. 14, and p. 28, l. 35 - p. 30, l. 20; preferably p. 30, l. 25 - p. 32, l. 30;

(DC-11): US 6,190,421 wherein extemporaneous mixtures of a composition (A) containing one or more oxidation dye precursors and optionally one or more couplers, of a composition (B), in powder form, containing one or more direct dyes (col. 5, l. 40 – col. 7, l. 14), optionally dispersed in an organic pulverulent excipient and/or a mineral pulverulent excipient, and a composition (C) containing one or more oxidizing agents are disclosed; formulations col. 8, l. 60 – col. 9, l. 56;

(DC-12): US 6,228,129, wherein a ready-to-use composition comprising at least one oxidation base, at least one cationic direct dye and at least one enzyme of the 2-electron oxidoreductase type in the presence of at least one donor for the said enzyme are disclosed; especially col. 8, l. 17 – col. 13, l. 65; dyeing formulations in col. 2, l. 16 to col. 25, l. 55, a multi-compartment dyeing device is described in col. 26, l. 13 - 24;

(DC-13): WO 99/20235, wherein compositions of at least one cationic dye and at least one nitrated benzene dye with cationic direct dyes and nitro benzene direct dyes are described; on p. 2, l. 1 to p. 7, l. 9, and p. 39, l. 1 to p. 40 l. 11, preferably p. 8, l. 12 to p. 25 l. 6, p. 26, l. 7 to p. 30, l. 15; p. 1, l. 25 to p. 8, l. 5, p. 30, l. 17 to p. 34 l. 25, p. 8, l. 12 to p. 25 l. 6, p. 35, l. 21 to 27, especially on p. 36, l. 1 to p. 37;

(DC-14): WO 99/20234, wherein compositions comprising at least one direct cationic dye and at least one autooxidisable dye, especially benzene, indol and indol. derivatives are described, preferably direct dyes on p. 2, l. 19 to p. 26, l. 4, and autooxidisable dyes as dislosed especially on p. 26, l. 10 to p. 28, l. 15; dyeing formulations especially on p. 34, l. 5 to p. 35, li 18;

(DC-15): EP 850 636, wherein oxidation dyeing compositions comprising at least one direct dye and at least one meta-aminophenol derivative as coupler component and at least

one developer compound and an oxidizing agent are disclosed, especially p. 5, l. 41 to p. 7, l. 52, dyeing formulations p. 19, l. 50 - p. 22, l. 12;

(DC-16): EP-A-850 637, wherein oxidation dyeing compositions comprising at least one oxidation base selected from para-phenylenediamines and bis(phenyl)alkylenediamines, and the acid-addition salts thereof, at least one coupler selected from meta-diphenols, and the acid-addition salts thereof, at least one cationic direct dye, and at least one oxidizing agent are disclosed, especially p. 6, l. 50 to p. 8, l. 44 are discloseded; dyeing formulations p. 21, l. 30 - p. 22, l. 57;

(DC-17): WO 99/48856, wherein oxidation dyeing compositions comprising cationic couplers are disclosed, especially p. 9, l. 16 - p. 13, l. 8, and p. 11, l. 20 - p. 12, l. 13; dyeing formulations p. 36, l. 7 – p. 39, l. 24;

(DC-18): DE 197 172 24, wherein dyeing agents comprising unsaturated aldehydes and coupler compounds and primary and secondary amino group compounds, nitrogen-containing heterocyclic compounds, amino acids, oligopeptids, aromatic hydroxy compounds, and/or at least one CH-active compound are disclosed p. 3, l. 42 - p. 5 l. 25; dyeing formulations p. 8, l. 25 – p. 9, l. 61.

In the dye combinations disclosed in the references (DC-01 – DC-18) above, the dyes of formula (1) according to the present invention may be added to the dye combinations or dyeing formulations or may be replaced with at least one dye of formula (1).

The present invention also releates to formulations, which are used for the dyeing of organic materials, preferably keratin-containing fibers, and most preferably human hair, comprising at least one dye of formula (1).

Preferably the dyes of formula (1) are incorporated into the composition for treating organic material, preferably for dyeing in amounts of 0.001 - 5% b.w. (hereinafter indicated merely by "%"), particularly 0.005 - 4%, more particularly 0.2 - 3%, based on the total weight of the composition.

The formulations may be applied on the keratin-containing fiber, preferably the human hair in different technical forms.

Technical forms of formulations are for example a solution, especially a thickened aqueous or aqueous alcoholic solution, a cream, foam, shampoo, powder, ~~a~~ gel, or ~~an~~ emulsion.

Customary the dyeing compositions are applied to the keratin-containing fiber in an amount of 50 to 100 g.

Preferred forms of formulations are ready-to-use compositions or multi-compartment dyeing devices or 'kits' or any of the multi-compartment packaging systems with compartments as described for example in US 6,190,421, col 2, l. 16 to 31.

The pH value of the ready-to-use dyeing compositions is usually from 2 to 11, preferably from 5 to 10.

Preferably the dyeing compositions, which are not stable to reduction, are prepared with oxidizing agent free compositions just before the dyeing process.

One preferred embodiment of the present invention relates to the formulation of dyes, wherein the dyes of formula (1) are in powder form.

Powder formulations are preferably used if stability and/or solubility problems as for example described in DE 197 13 698, p. 2, l. 26 to 54 and p. 3, l. 51 to p. 4, l. 25, and p. 4, l. 41 to p. 5 l. 59.

Suitable cosmetic hair-care formulations are hair-treatment preparations, e.g. hair-washing preparations in the form of shampoos and conditioners, hair-care preparations, e.g. pre-treatment preparations or leave-on products such as sprays, creams, gels, lotions, mousses and oils, hair tonics, styling creams, styling gels, pomades, hair rinses, treatment packs, intensive hair treatments, hair-structuring preparations, e.g. hair-waving preparations for permanent waves (hot wave, mild wave, cold wave), hair-straightening preparations, liquid hair-setting preparations, hair foams, hairsprays, bleaching preparations, e.g. hydrogen peroxide solutions, lightening shampoos, bleaching creams, bleaching powders, bleaching pastes or oils, temporary, semi-permanent or permanent hair colorants, preparations containing self-oxidizing dyes, or natural hair colorants, such as henna or camomile.

For use on human hair, the dyeing compositions of the present invention can usually be incorporated into an aqueous cosmetic carrier. Suitable aqueous cosmetic carriers include, for example W/O, O/W, O/W/O, W/O/W or PIT emulsions and all kinds of microemulsions, creams, sprays, emulsions, gels, powders and also surfactant-containing foaming solutions, e.g. shampoos or other preparations, that are suitable for use on keratin-containing fibers. Such forms of use are described in detail in Research Disclosure 42448 (August 1999). If necessary, it is also possible to incorporate the dyeing compositions into anhydrous carriers, as described, for example, in US-3 369 970, especially col 1, l. 70 to col 3, l. 55. The dyeing compositions according to the invention are also excellently suitable for the dyeing method described in DE-A-3 829 870 using a dyeing comb or a dyeing brush.

The constituents of the aqueous carrier are present in the dyeing compositions of the present invention in the customary amounts, for example emulsifiers may be present in the dyeing compositions in concentrations ~~of~~ from 0.5 to 30 % b.w. and thickeners in concentrations ~~of~~ from 0.1 to 25 % b.w. of the total dyeing composition.

Further carriers for dying compositions are for example described in "Dermatology", edited by Ch. Culnan, H. Maibach, Verlag Marcel Dekker Inc., New York, Basle, 1986, Vol. 7, Ch. Zviak, The Science of Hair Care, chapter 7, p. 248-250, especially on p. 243, l. 1 to p. 244, l. 12.

A shampoo has, for example, the following composition:
0.01 to 5 % b.w. of a dye of formula (1);
8 % b.w of disodium PEG-5 laurylcitrate Sulfosuccinate, Sodium Laureth Sulfate;
20 % b.w. of sodium cocoamphoacetate;
0.5 % b.w. of methoxy PEG/PPG-7/3 aminopropyl dimethicone;
0.3 % b.w. of hydroxypropyl guar hydroxypropytrimonium chloride;
2.5 % b.w. of PEG-200 hydrogenated glyceryl palmate; PEG-7 glyceryl cocoate;
0.5 % b.w. of PEG-150 distearate;
2.2. % b.w of citric acid;
perfume, preservatives; and
water ad 100 %.

The dyes of formula (1) may be stored in a liquid to paste-like preparation (aqueous or non-aqueous) or in the form of a dry powder.

When the dyes and adjuvants are stored together in a liquid preparation, the preparation should be substantially anhydrous in order to reduce reaction of the compounds.

The dyeing compositions according to the invention may comprise any active ingredients, additives or adjuvants known for such preparations, like surfactants, solvents, bases, acids, perfumes, polymeric adjuvants, thickeners and light stabilisers.
The following adjuavents are preferably used in the hair dyeing compositions of the present invention:

- non-ionic polymers, for example vinylpyrrolidone/vinyl acrylate copolymers, polyvinyl-pyrrolidone and vinylpyrrolidone/vinyl acetate copolymers and polysiloxanes;
- cationic polymers, such as quaternised cellulose ethers, polysiloxanes having quaternary groups, dimethyldiallylammonium chloride polymers, copolymers of dimethyldiallyl-ammonium chloride and acrylic acid, as available commercially under the name Merquat® 280 and the use thereof in hair dyeing as described, for example, in DE-A-4 421 031, especially p. 2, l. 20 to 49, or EP-A-953 334;
- acrylamide/dimethyldiallylammonium chloride copolymers, diethyl-sulfate-quaternised dimethylaminoethyl methacrylate/vinylpyrrolidone copolymers, vinylpyrrolidone/-imidazolinium methochloride copolymers;
- quaternised polyvinyl alcohol:
- zwitterionic and amphoteric polymers, such as acrylamido-propyltrimethylammonium chloride/acrylate copolymers and octylacrylamide/methyl methacry-late/tert-butylaminoethyl methacrylate/2-hydroxypropyl methacrylate copolymers;
- anionic polymers, such as, for example, polyacrylic acids, crosslinked polyacrylic acids, vinyl acetate/crotonic acid copolymers, vinylpyrrolidone/vinyl acrylate copolymers, vinyl acetate/butyl maleate/isobornyl acrylate copolymers, methyl vinyl ether/maleic anhydride copolymers and acrylic acid/ethyl acrylate/N-tert-butyl acrylamide terpolymers;
- thickeners, such as agar, guar gum, alginates, xanthan gum, gum arabic, karaya gum, locust bean flour, linseed gums, dextrans, cellulose derivatives, e.g. methyl cellulose, hydroxyalkyl cellulose and carboxymethyl cellulose, starch fractions and derivatives, such amylose, amylopectin and dextrins, clays, e.g. bentonite or fully synthetic hydro-colloids such as, for example, polyvinyl alcohol;

- structuring agents, such as glucose and maleic acid;
- hair-conditioning compounds, such as phospholipids, for example soya lecithin, egg lecithin, cephalins, silicone oils, and conditioning compounds, such as those described in DE-A-19 729 080, especially p. 2, l. 20 to 49, EP-A-834 303, especially p. 2, l. 18 - p. 3, l. 2, or EP-A-312 343, especially p. 2, l. 59 - p. 3, l. 11;
- protein hydrolysates, especially elastin, collagen, keratin, milk protein, soya protein and wheat protein hydrolysates, condensation products thereof with fatty acids and also quaternised protein hydrolysates;
- perfume oils, dimethyl isosorbitol and cyclodextrins,
- solubilisers, such as ethanol, isopropanol, ethylene glycol, propylene glycol, glycerol and diethylene glycol,
- anti-dandruff active ingredients, such as piroctones, olamines and zinc Omadine,
- substances for adjusting the pH value;
- panthenol, pantothenic acid, allantoin, pyrrolidonecarboxylic acids and salts thereof, plant extracts and vitamins;
- cholesterol;
- light stabilisers and UV absorbers as listed in Table below:

Table 1: UV absorbers which may be use in the dyeing compositions of the present invention

No.	Chemical Name	CAS No.
1	(+/-)-1,7,7-trimethyl-3-[(4-methylphenyl)methylene]bicyclo-[2.2.1]heptan-2-one	36861-47-9
2	1,7,7-trimethyl-3-(phenylmethylene)bicyclo[2.2.1]heptan-2-one	15087-24-8
3	(2-Hydroxy-4-methoxyphenyl)(4-methylphenyl)methanone	1641-17-4
4	2,4-dihydroxybenzophenone	131-56-6
5	2,2',4,4'-tetrahydroxybenzophenone	131-55-5
6	2-Hydroxy-4-methoxy benzophenone;	131-57-7
7	2,2'-dihydroxy-4,4'-dimethoxybenzophenone	131-54-4
8	2,2'-Dihydroxy-4-methoxybenzophenone	131-53-3
9	1-[4-(1,1-dimethylethyl)phenyl]-3-(4-methoxyphenyl)propane-1,3-dione	70356-09-1
10	3,3,5-Trimethyl cyclohexyl-2-hydroxy benzoate	118-56-9
11	Isopentyl p-methoxycinnamate	71617-10-2
12	Menthyl-o-aminobenzoate	134-09-8
13	Menthyl salicylate	89-46-3

Table 1: UV absorbers which may be use in the dyeing compositions of the present invention

No.	Chemical Name	CAS No.
14	2-Ethylhexyl 2-cyano,3,3-diphenylacrylate	6197-30-4
15	2- ethylhexyl 4- (dimethylamino)benzoate	21245-02-3
16	2- ethylhexyl 4- methoxycinnamate	5466-77-3
17	2- ethylhexyl salicylate	118-60-5
18	Benzoic acid, 4, 4', 4"-(1, 3, 5- triazine-2, 4,6-triyltriimino)tris-,tris(2-ethylhexyl)ester; 2,4,6-Trianilino-(p-carbo-2'-ethylhexyl-1'-oxi)-1,3,5-triazine	88122-99-0
19	Benzoic acid, 4-amino-, ethyl ester, polymer with oxirane	113010-52-9
20	2-Propenamide, N-[[4-[(4,7,7-trimethyl-3-oxobicyclo[2.2.1]hept-2-ylidene)methyl]phenyl]methyl]-, homopolymer	147897-12-9
21	Triethanolamine salicylate	2174-16-5
22	2,2'-Methylene-bis-[6-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethyl-butyl)-phenol]	103597-45-1
23	2,4-bis{[4-(2-ethylhexyloxy)-2-hydroxy]-phenyl}-6-(4-methoxyphenyl)-(1,3,5)-triazine (Tinosorb S)	187393-00-6
24	Benzoic acid, 4,4'-[[6-[[4-[[(1,1-dimethylethyl)amino]carbonyl]-phenyl]amino]1,3,5-triazine-2,4-diyl]diimino]bis-, bis(2-ethylhexyl)-ester	154702-15-5
25	Phenol, 2-(2H-benzotriazol-2-yl)-4-methyl-6-[2-methyl-3-[1,3,3,3-tetramethyl-1-[(trimethylsilyl)oxy]disiloxanyl]propyl]-	155633-54-8
26	Dimethicodiethylbezalmalonate	207574-74-1
27	Benzoic acid, 2-[4-(diethylamino)-2-hydroxybenzoyl]-, hexyl ester	302776-68-7
28	1,3,5-Triazine, 2,4,6-tris(4-methoxyphenyl)-	7753-12-0
29	1,3,5-Triazine, 2,4,6-tris[4-[(2-ethylhexyl)oxy]phenyl]-	208114-14-1
30	2-Propenoic acid, 3-(1H-imidazol-4-yl)-	104-98-3
31	Benzoic acid, 2-hydroxy-, [4-(1-methylethyl)phenyl]methyl ester	94134-93-7
32	1,2,3-Propanetriol, 1-(4-aminobenzoate)	136-44-7
33	Benzeneacetic acid, 3,4-dimethoxy-a-oxo-	4732-70-1
34	2-Propenoic acid, 2-cyano-3,3-diphenyl-, ethyl ester	5232-99-5
35	Anthralinic acid, p-menth-3-yl ester	134-09-8
36	1,3,5-Triazine-2,4,6-triamine, N,N'-bis[4-[5-(1,1-dimethylpropyl)-2-benzoxazolyl]phenyl]-N"-(2-ethylhexyl)- or Uvasorb K2A	288254-16-0
37	2-Hydroxy-4-methoxy benzophenone-5-sulfonic acid	4065-45-6
38	Alpha-(2-oxoborn-3-ylidene)toluene-4-sulphonic acid and its salts	56039-58-8
39	Methyl N,N,N-trimethyl-4-[(4,7,7-trimethyl-3-oxobicyclo[2,2,1]hept-2-ylidene)methyl]anilinium sulphate;	52793-97-2

Table 1: UV absorbers which may be use in the dyeing compositions of the present invention		
No.	Chemical Name	CAS No.
40	4- aminobenzoic acid	150-13-0
41	2- phenyl- 1H- benzimidazole- 5- sulphonic acid	27503-81-7
42	3, 3'- (1, 4- phenylenedimethylene)bis[7, 7- dimethyl- 2- oxo-bicyclo[2.2.1]heptane- 1- methanesulfonic acid]	90457-82-2
43	1H-Benzimidazole-4,6-disulfonic acid, 2,2'-(1,4-phenylene)bis-, disodium salt	180898-37-7
44	Benzenesulfonic acid, 3-(2H-benzotriazol-2-yl)-4-hydroxy-5-(1-methylpropyl)-, monosodium salt	92484-48-5
45	1-Dodecanaminium, N-[3-[[4-(dimethylamino)benzoyl]amino]-propyl]N,N-dimethyl-, salt with 4-methylbenzenesulfonic acid (1:1)	156679-41-3
46	1-Propanaminium, N,N,N-trimethyl-3-[(1-oxo-3-phenyl-2-propenyl)-amino]-, chloride	177190-98-6
47	1H-Benzimidazole-4,6-disulfonic acid, 2,2'-(1,4-phenylene)bis-	170864-82-1
48	1-Propanaminium, 3-[[3-[3-(2H-benzotriazol-2-yl)-5-(1,1-dimethyl-ethyl)-4-hydroxyphenyl]-1-oxopropyl]amino]-N,N-diethyl-N-methyl-, methyl sulfate (salt)	340964-15-0
49	2,2'-bis(1,4-phenylene)-1H-benzimidazole-4,6-disulphonic acid mo-no sodium salt or Disodium phenyl dibenzimidazole tetrasulfonate or Neoheliopan AP	349580-12-7,

The use of UV absorbers can effectively protect natural and dyed hair from the damaging rays of the sun and increase the wash fastness of dyed hair.

Furthermore, the following UV absorbers or combinations may be used in the dyeing compositions according to the invention:

- cationic benzotriazole UV absorbers as for example described in WO 01/36396 especially on p. 1, l. 20 to p. 2, l. 24, and preferred on p. 3 to 5, and on p. 26 to 37;
- cationic benzotriazole UV in combination with antioxidants as described in WO 01/36396, especially on p. 11, l. 14 to p. 18;
- UV absorbers in combination with antioxidants as described in US Patent 5 922 310, especially in col 2, l. 1 to 3;
- UV absorbers in combination with antioxidants as described in US Patent 4 786 493, especially in col 1, 42 to col 2, l. 7, and preferred in col 3, 43 to col 5, l. 20;
- combination of UV absorbers as described in US Patent 5 830 441, especially in col 4, l. 53 to 56;
- combination of UV absorbers as described in WO 01/36396, especially on p. 11, l. 9 to 13; or

- triazine derivatives as described in WO 98/22447, especially on p. 1, l. 23 to p. 2, l. 4, and preferred on p. 2, l. 11 to p. 3, l. 15 and most preferred on p. 6 to 7, and 12 to 16. Suitable cosmetic preparations may usually contain ~~from~~ 0.05 to 40 % b.w., preferably from 0.1 to 20 % b.w., based on the total weight of the composition, of one or more UV absorbers;
- consistency regulators, such as sugar esters, polyol esters or polyol alkyl ethers;
- fats and waxes, such as spermaceti, beeswax, montan wax, paraffins, fatty alcohols and fatty acid esters;
- fatty alkanolamides;
- polyethylene glycols and polypropylene glycols having a molecular weight of from 150 to 50 000, for example such as those described in EP-A-801 942, especially p. 3, l. 44 to 55,
- complexing agents, such as EDTA, NTA and phosphonic acids,
- swelling and penetration substances, such as polyols and polyol ethers, as listed extensively, for example, in EP-A-962 219, especially p. 27, l. 18 to 38, for example glycerol, propylene glycol, propylene glycol monoethyl ether, butyl glycol, benzyl alcohol, carbonates, hydrogen carbonates, guanidines, ureas and also primary, secondary and tertiary phosphates, imidazoles, tannins, pyrrole;
- opacifiers, such as latex;
- pearlising agents, such as ethylene glycol mono- and di-stearate;
- propellants, such as propane-butane mixtures, N_2O, dimethyl ether, CO_2 and air;
- antioxidants; preferably the phenolic antioxidants and hindered nitroxyl compounds disclosed in ip.com (IPCOM # 000033153D);
- sugar-containing polymers, as described in EP-A-970 687;
- quaternary ammonium salts, as described in WO 00/10517;
- Bacteria inhibiting agents, like preservatives that have a specific action against gram-positive bacteria, such as 2,4,4'-trichloro-2'-hydroxydiphenyl ether, chlorhexidine (1,6-di(4-chlorophenyl-biguanido)hexane) or TCC (3,4,4'-trichlorocarbanilide). A large number of aromatic substances and ethereal oils also have antimicrobial properties. Typical examples are the active ingredients eugenol, menthol and thymol in clove oil, mint oil and thyme oil. A natural deodorising agent of interest is the terpene alcohol farnesol (3,7,11-trimethyl-2,6,10-dodecatrien-1-ol), which is present in lime blossom oil. Glycerol monolaurate has also proved to be a bacteriostatic agent. The amount of the additional

bacteria-inhibiting agents present is usually from 0.1 to 2 % b.w., based on the solids content of the preparations;

The dyeing compositions according to the present invention generally comprise at least one surfactant.
Suitable surfactants are zwitterionic or ampholytic, or more preferably anionic, non-ionic and/or cationic surfactants.

Suitable anionic surfactants in the dyeing compositions according to the present invention include all anionic surface-active substances that are suitable for use on the human body. Such substances are characterised by an anionic group that imparts water solubility, for example a carboxylate, sulfate, sulfonate or phosphate group, and a lipophilic alkyl group having approximately 10 to 22 carbon atoms. In addition, glycol or polyglycol ether groups, ester, ether and amide groups and also hydroxy groups may be present in the molecule. The following are examples of suitable anionic surfactants, each in the form of sodium, potassium or ammonium salts or mono-, di- or tri-alkanolammonium salts having 2 or 3 carbon atoms in the alkanol group:

- linear fatty acids having 10 to 22 carbon atoms (soaps),
- ether carboxylic acids of formula R-O-$(CH_2$-CH_2-$O)_x$-CH_2-COOH, in which R is a l.ar alkyl group having 10 to 22 carbon atoms and x = 0 or from 1 to 16,
- acyl sarcosides having 10 to 18 carbon atoms in the acyl group,
- acyl taurides having 10 to 18 carbon atoms in the acyl group,
- acyl isothionates having 10 to 18 carbon atoms in the acyl group,
- sulfosuccinic mono- and di-alkyl esters having 8 to 18 carbon atoms in the alkyl group and sulfosuccinic monoalkylpolyoxyethyl esters having 8 to 18 carbon atoms in the alkyl group and from 1 to 6 oxyethyl groups,
- linear alkane sulfonates having 12 to 18 carbon atoms,
- linear α-olefin sulfonates having 12 to 18 carbon atoms,
- α-sulfo fatty acid methyl esters of fatty acids having12 to 18 carbon atoms,
- alkyl sulfates and alkyl polyglycol ether sulfates of formula R'-O$(CH_2$-CH_2-$O)_{x'}$-SO_3H, in which R' is a preferably l.ar alkyl group having 10 to 18 carbon atoms and x' = 0 or from 1 to 12,
- mixtures of surface-active hydroxysulfonates according to DE-A-3 725 030;

- sulfated hydroxyalkylpolyethylene and/or hydroxyalkylenepropylene glycol ethers according to DE-A-3 723 354, especially p. 4, l. 42 to 62,
- sulfonates of unsaturated fatty acids having 12 to 24 carbon atoms and 1 to 6 double bonds according to DE-A-3 926 344, especially p. 2, l. 36 to 54,
- esters of tartaric acid and citric acid with alcohols which are addition products of approximately from 2 to 15 molecules of ethylene oxide and/or propylene oxide with fatty alcohols having from 8 to 22 carbon atoms, or
- anionic surfactants, as described in WO 00/10518, especially p. 45, l. 11 to p. 48, l. 3.

Preferred anionic surfactants are alkyl sulfates, alkyl polyglycol ether sulfates and ether carboxylic acids having 10 to 18 carbon atoms in the alkyl group and up to 12 glycol ether groups in the molecule, and also especially salts of saturated and especially unsaturated C_8-C_{22}carboxylic acids, such as oleic acid, stearic acid, isostearic acid and palmitic acid.

Surface-active compounds that carry at least one quaternary ammonium group and at least one $-COO^-$ or $-SO_3^-$ group in the molecule are terminated zwitterionic surfactants. Preference is given the so-called betaines, such as the N-alkylN,N-dimethylammonium glycinates, for example cocoalkyldimethylammonium glycinate, N-acylaminopropyl-N,N-dimethylammonium glycinates, for example cocoacylaminopropyldimethylammonium glycinate, and 2-alkyl-3-carboxymethyl-3-hydroxyethylimidazol. having from 8 to 18 carbon atoms in the alkyl or acyl group and also cocoacylaminoethylhydroxyethylcarboxymethyl glycinate. A preferred zwitterionic surfactant is the fatty acid amide derivative known by the CTFA name cocoamidopropyl betaine.

Ampholytic surfactants are surface-active compounds that, in addition to a C_8-C_{18}-alkyl or -acyl group and contain at least one free amino group and at least one -COOH or $-SO_3H$ group in the molecule and are capable of forming internal salts. Examples of suitable ampholytic surfactants include N-alkylglycines, N-alkylpropionic acids, N-alkylaminobutyric acids, N-alkyliminodipropionic acids, N-hydroxyethyl-N-alkylamidopropylglycines, N-alkyltaurines, N-alkylsarcosines, 2-alkylaminopropionic acids and alkylaminoacetic acids, each having approximately from 8 to 18 carbon atoms in the alkyl group. Ampholytic surfactants to which special preference is given are N-cocoalkylaminopropionate, cocoacylaminoethylaminopropionate and C_{12}-C_{18}acylsarcosine.

Suitable non-ionic surfactants are described in WO 00/10519, especially p. 45, l. 11 to p. 50, l. 12. Non-ionic surfactants contain as hydrophilic group, for example, a polyol group, a polyalkylene glycol ether group or a combination of polyol and polyglycol ether groups. Such compounds are, for example:

- addition products of 2 to 30 mol of ethylene oxide and/or 0 to 5 mol of propylene oxide with l.ar fatty alcohols having 8 to 22 carbon atoms, with fatty acids having 12 to 22 carbon atoms and with alkylphenols having 8 to 15 carbon atoms in the alkyl group,
- C_{12}-C_{22} fatty acid mono- and di-esters of addition products of 1 to 30 mol of ethylene oxide with glycerol,
- C_8-C_{22}alkyl-mono- and -oligo-glycosides and ethoxylated analogues thereof,
- addition products of 5 to 60 mol of ethylene oxide with castor oil and hydrogenated castor oil,
- addition products of ethylene oxide with sorbitan fatty acid esters,
- addition products of ethylene oxide with fatty acid alkanolamides.

The surfactants which are addition products of ethylene and/or propylene oxide with fatty alcohols or derivatives of such addition products may either be products having a "normal" homologue distribution or products having a restricted homologue distribution. "Normal" homologue distribution are mixtures of homologues obtained in the reaction of fatty alcohol and alkylene oxide using alkali metals, alkali metal hydroxides or alkali metal alcoholates as catalysts. Restricted homologue distributions, on the other hand, are obtained when, for example, hydrotalcites, alkali metal salts of ether carboxylic acids, alkali metal oxides, hydroxides or alcoholates are used as catalysts.

The use of products having restricted homologue distribution may be preferred.

Examples of cationic surfactants that can be used in the dyeing compositions according to the invention are especially quaternary ammonium compounds. Preference is given to ammonium halides, such as alkyltrimethylammonium chlorides, dialkyldimethylammonium chlorides and trialkylmethylammonium chlorides, for example cetyltrimethylammonium chloride, stearyltrimethylammonium chloride, distearyldimethy-lammonium chloride, lauryldimethylammonium chloride, lauryldimethylbenzylammonium chloride and tricetyl-methylammonium chloride. Further cationic surfactants that can be used in accordance with the invention are quaternised protein hydrolysates.

Also suitable are cationic silicone oils, such as, for example, the commercially available products Q2-7224 (manufacturer: Dow Corning; a stabilised trimethylsilylamodimethicone), Dow Corning 929 emulsion (comprising a hydroxylamino-modified silicone, which is also referred to as amodimethicone), SM-2059 (manufacturer: General Electric), SLM-55067 (manufacturer: Wacker) and also Abil®-Quat 3270 and 3272 (manufacturer: Th. Goldschmidt; diquaternary polydimethylsiloxanes, quaternium-80), or silicones, as described in WO 00/12057, especially p. 45, l. 9 to p. 55, l. 2.

Alkylamidoamines, especially fatty acid amidoamines, such as the stearylamidopropyldimethylamine obtainable under the name Tego Amid® 18 are alos preffered as surfactants in the present dyeing compositions. They are distinguished not only by a good conditioning action but also especially by their good biodegradability.

Quaternary ester compounds, so-called "esterquats", such as the methyl hydroxyalkyldialkoyloxyalkylammonium methosulfates marketed under the trademark Stepantex®, are also very readily biodegradable.

An example of a quaternary sugar derivative that can be used as cationic surfactant is the commercial product Glucquat®100, according to CTFA nomenclature a "lauryl methyl gluceth-10 hydroxypropyl dimonium chloride".

The alkyl-group-containing compounds used as surfactants may be single substances, but the use of natural raw materials of vegetable or animal origin is generally preferred in the preparation of such substances, with the result that the substance mixtures obtained have different alkyl chain lengths according to the particular starting material used.

The dyes of formula (1) are suitable for the dyeing of organic material, perferably keratin-containig fibers.

A further preferred embodiment of the present invention relates to a method of treating keratin-containig fibers with sulfide dyes of formula (1).

The method comprises treating the hair in the presence of a reduction agent.

Preferred reduction agents are for example thioglycol acid or salts therof, gycerine monothioglycolat, cystein, 2-mercaptopropionic acid, 2-mercaptoethylamine, thiolactic acid, thioglycerine, sodium sulfite, dithionithe, ammonium sulfite, sodium bisulfite, sodium metabisulfite or hydrochinon.

In addition, the present invention relates to a method of

a. treating the keratin-containing fibers with a compound of formula (1),
b. wearing the coloured hair for the desired period of time,
c. removing the colour applied in step a) from hair by contacting the hair with an aqueous based colour removal composition containg a reduction agent capable of disrupting the –S-S-bonds between the dye molecule and the hair fiber surface to cause the dye molcule to become disassociated from the hair fiber.

Further, the present invention concerns a process, comprising treating the hair with

a. a reduction agent, and
b. at least a single sulfide dye of formula (1) as defined above, and optionally
c. with an oxidizing agent.

The sequence of the reaction steps is generally not important, the reduction agent can be applied first or in a final step.

Preferred is a process, which comprises treating the hair

a_1) with at least one single dye of formula (1), and
b_1) then with a reduction agent; or

a process, which comprises contacting hair

a_2) with a reduction agent and
b_2) then with at least one single sulfide dye of formula (1) as defined above.

In the present invention preferred is further a process, which comprises contacting hair

a) with a reduction agent,
b) then with at least one dye of formula (1), and
c) then with an oxidizing agent.

A further process of the present invention comprises contacting hair
a) with at least one single dye of formula (1), and
b) then with a reduction agent, and
c) then with an oxidizing agent.

Usally, the oxidizing agent is applied together with an acid or a base.

The acid is for example citric acid, phosphoric acid or tartrate acid.
The base is for example sodium hydroxide, ammonia or monoethanolamine.

Usually, the dyeing compositions are ~~usually~~ applied to the keratin-containg fiber in an amount of from 50 to 100 g.

The dyes of formula (1) are suitable for all-over dyeing of the hair, that is to say when dyeing the hair on a first occasion, and also for re-dyeing subsequently, or dyeing of locks or parts of the hair.

The dyes of formula (1) are applied ~~to~~ on the hair for example by massage with the hand, a comb, a brush, or a bottle, or a bottle, which is combined with a comb or a nozzle.

In the processes for dyeing according to the invention, whether or not dyeing is to be carried out in the presence of a further dye will depend upon the color shade to be obtained.

Further preferred is a process for dyeing keratin-containing fibers which comprises treating the keratin-containing fiber with at least one dye of formula (1), a base and an oxidizing agent.

The oxidation dyeing process usually involves lightening, that is to say that it involves applying to the keratin-containing fibers, at basic pH, a mixture of bases and aqueous hydrogen peroxide solution, leaving the applied mixture to stand on the hair and then rinsing the hair. It allows, particularly in the case of hair dyeing, the melanin to be lightened and the hair to be dyed.

Lightening the melanin has the advantageous effect of creating a unified dyeing in the case of grey hair, and, in the case of naturally pigmented hair, of bringing out the color, that is to say of making it more visible.

In general, the oxidizing agent containing composition is left on the fiber for 0 to 15 minutes, in particular for 0 to 5 minutes at 15 to 45°C, usually in amounts of 30 to 200 g.

Oxidizing agents are for example persulfate or dilute hydrogen peroxide solutions, hydrogen peroxide emulsions or hydrogen peroxide gels, alkal. earth metal peroxides, organic peroxides, such as urea peroxides, melamine peroxides, or alkalimetalbromat fixations are also applicable if a shading powder on the basis of semi-permanent, direct hair dyes is used.

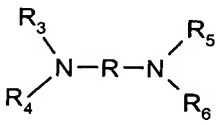
Further preferred oxidizing agents are

- oxidizing agents to achieve lightened coloration, as described in WO 97/20545, especially p. 9, *l.* 5 to 9,
- oxidizing agents in the form of permanent-wave fixing solution, as described in DE-A-19 713 698 , especially p. 4, l. 52 to 55, and l. 60 and 61 or EP-A-1062940, especially p. 6, l. 41 to 47 (and in the equivalent WO 99/40895).

Most preferred oxidizing agent is hydrogen peroxide, preferably used in a concentration from about 2 to 30 %, more preferably about 3 to 20% by, and most preferably from 6 to 12% b.w. the corresponding composition.

The oxidizing agents may be present in the dyeing compositions according to the invention preferably in an amount from 0.01 % to 6 %, especially from 0.01 % to 1 %, based on the total dyeing composition.

In general, the dyeing with an oxidative agent is carried out in the presence of a base, for example ammonia, alkali metal carbonates, earth metal (potassium or lithium) carbonates, alkanol amines, such as mono-, di- or triethanolamine, alkali metal (sodium) hydroxides, earth metal hydroxides or compounds of the formula



, wherein

R is a propylene residue, which may be substituted with OH or C_1-C_4alkyl,
R_3, R_4, R_5 and R_6 are independently or dependently from each other hydrogen, C_1-C_4alkyl or hydroxy-(C_1-C_4)alkyl.

The pH-value of the oxidizing agent containing composition is usually about 2 to 7, and in particular about 2 to 5.

One preferred method of applying formulations comprising the dyes of formula (1) on the keratin-containing fiber, preferably the hair is by using a multi-compartment dyeing device or "kit" or any other multi-compartment packaging system, as described for example in WO 97/20545 on p. 4, l. 19 to l. 27.

The first compartment contains for examle at least one dye of formula (1) and optionally furhter direct dyes and a basifying agent, and in the second compartment an oxidizing agent; or in the first compartment at least one dye of formula (1) and optionally futhter direct dyes, in the second compartment a basifiying agent and in the third compartment an oxidizing agent.

Generally the hair is rinsed after treatment with the dyeing solution and/or permanent-wave solution.

A further preferred embodiment of the present invention relates to a method of dyeing hair with oxidative dyes, which comprises

a. mixing at least one dye of formula (1) and optionally at least one coupler compound and at least one developer compound, and an oxidizing agent, which optionally contains at least one further dye, and
b. contacting the keratin-containing fibers with the mixture as prepared in step a.

The pH-value of the oxidizing agent free composition is usually from 3 to 11, and in particular from 5 to 10, and most particular about 9 to 10.

Preferably, a ready-to-use composition is prepared according to a first preferred embodiment by a process which comprises a preliminary step which involves separately storing, on the one hand, a composition (A) comprising, in a medium which is suitable for dyeing, at least one developer compound, especially selected from para-phenylenediamines and bis(phenyl)-

alkylenediamines, and the acid-addition salts thereof, at least one coupler, especially selected from meta-phenylenediamines and the acid-addition salts thereof, and at least one dye of formula (1), on the other hand, a composition (B) containing, in a medium which is suitable for dyeing, at least one oxidizing agent and mixing (A) and (B) together immediately before applying this mixture to the keratin-containing fibers.

According to a second preferred embodiment for the preparation of the ready-to-use dye composition, the process includes a preliminary step which involves separately storing, on the one hand, a composition (A) comprising, in a medium which is suitable for dyeing, at least one developer compound, especially selected from para-phenylenediamines and bis(phenyl)alkylenediamines, and the acid-addition salts thereof, at least one coupler compound, especially selected from meta-phenylenediamines and the acid-addition salts thereof; on the other hand, a composition (A') comprising, in a medium which is suitable for dyeing, at least one dye of formula (1), and, finally, a composition (B) containing, in a medium which is suitable for dyeing, at least one oxidizing agent as defined above, and mixing them together at the time of use immediately before applying this mixture to the keratin-containing fibers.

The composition (A') used according to this second embodiment may optionally be in powder form, the dye(s) of formula (1) (themselves) constituting, in this case, all of the composition (A') or optionally being dispersed in an organic and/or inorganic pulverulent excipient.

When present in the composition A', the organic excipient may be of synthetic or natural origin and is selected in particular from crosslinked and non-crosslinked synthetic polymers, polysaccharides such as celluloses and modified or unmodified starches, as well as natural products such as sawdust and plant gums (guar gum, carob gum, xanthan gum, etc.).

When present in the composition (A'), the inorganic excipient may contain metal oxides such as titanium oxides, aluminium oxides, kaolin, talc, silicates, mica and silicas.

An very suitable excipient in the dyeing compositions according to the invention is sawdust.

The powdered composition (A') may also contain binders or coating products in an amount which preferably does not exceed approximately 3% b.w. relative to the total weight of

composition (A'). These binders are preferably selected from oils and liquid fatty substances of inorganic, synthetic, animal or plant origin.

Furthermore, the present invention relates to a process of dyeing of keratin-containig fibers of the dyes of formula (1) with autooxidable compounds and optionally further dyes.

Furthermore, the present invention relates to a process for dyeing keratin-containig fibers with the dyes of formula (1) and capped diazotised compounds, which comprises,

a. treating the keratin-containing fibers under alkal. conditions with at least one capped diazotised compound and a coupler compound, and optionally a developer compound ad optionally an oxidizing agent, and optionally in the presence of a further dye, and optionally with at least one dye of formula (1); and
b. adjusting the pH in the range of 6 to 2 by treatment with an acid, optionally in the presence of a further dye, and optionally at least one dye of formula (1),

with the proviso that at least in one step a. or b. at least one dye of formula (1) is present.

The capped diazotised compound and coupler compound and optionally the oxidizing agent and developer compound can be applied in any desired order successively, or simultaneously.

Preferably, the capped diazotised compound and the coupler compound are applied simultaneously, in a single composition.

"Alkal. conditions" denotes a pH in the range from 8 to 10, preferably 9-10, especially 9.5-10, which are chieved by the addition of bases, for example sodium carbonate, ammonia or sodium hydroxide.

The bases may be added to the hair, to the dye precursors, the capped diazotised compound and/or the water-soluble coupling component, or to the dyeing compositions comprising the dye precursors.

Acids are for example tartaric acid or citric acid, a citric acid gel, a suitable buffer solution with optionally an acid dye.

The ratio of the amount of alkal. dyeing composition applied in the first stage to that of acid dyeing composition applied in the second stage is preferably about from 1:3 to 3:1, especially about 1:1.

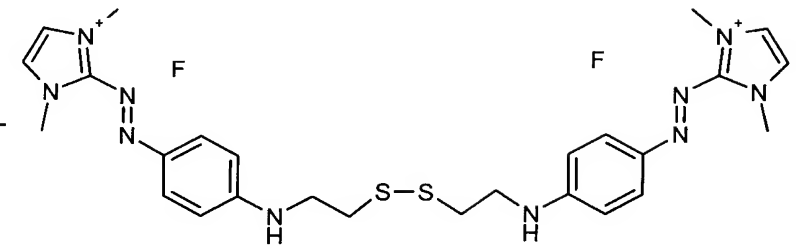
Furthermore, the present invention relates to a process for dyeing keratin-containig fibers with the dyes of formula (1) and at least one acid dye.

The following Examples serve to illustrate the processes for dyeing without limiting the processes thereto. Unless specified otherwise, parts and percentages relate to weight. The amounts of dye specified are relative to the material being coloured.
T, s, d, q and J, wherein t is a triplett, s is singulett, d is duplett, q is a quartett, and J is a coupling constant, define the NMRspectra values.

Examples A - Process of Preparation

Example A1

(101)

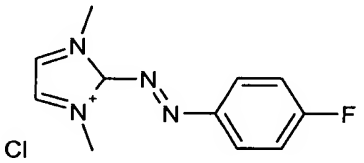


12.4 g 4-fluoroanilin are added to a stirred solution of 25 ml water and 25 ml of 32% hydrochloric acid at 295 K. The reaction mixture is cooled to 273 K and 19 ml of a 36% sodium nitrite solution are dropped at such a rate that the temperature of the mixture is maintained in the range of 273 to 276 K. After the addition of the sodium nitrite solution the mixture is stirred for one hour. If no excess of nitrite is detected during one hour (detection by using a potassium iodide paper) further sodium nitrite solution is added. The remaining excess of nitrite is reduced with sulfamic acid. The obtained diazo solution is dropped to a 273 K cold solution of 7.4 g imidazole in 30 ml water, whereby the pH of the solution is maintained in the range of pH 10 to 11 by adding 36% of asodium hydroxide solution. After completing the diazo addition the obtained suspension is warmed up to 295 K, the pH is adjusted to 10.5 with 36% sodium hydroxide solution. After stirring for one hour at this pH and temperature the suspension is filtered off and washed twice with 50 ml water to obtain 55 g of a humid product, which is suspended in 200 ml water and 3 weight equivalents dimethyl sulfate and sodium hydroxide are simultaneously added for maintaining the pH at 10-10.3 and the temperature at 298-303K.

The reaction is allowed to stand for one more hour to finish the hydrolysis of excess of dimethyl sulfate.

100 g sodium chloride and 50 g potassium chloride are added at 273K and allowed to stand for 16 hours. The product is separated by filtration and washed with a cold solution of sodium /potassium chloride. About 20g of the compound of formula

(101a)



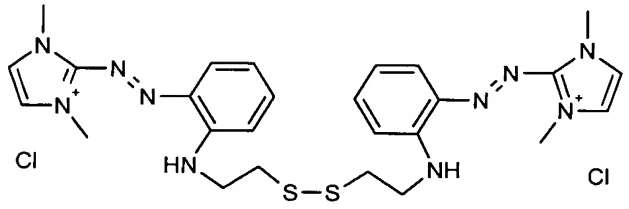
are obtained

6.9 g of cisteamine dihydrochloride are added at 293 K under nitrogen atmosphere to 20 g of the compound of formula (101a) in 120g isopropanol and 24 g triethylamine. The temperature is raised to 333 K and the reaction mixture is stirred at this temperature during 25 hours. The reaction mass is stirred for 4 hours while the temperature is decreased to 295 K. The reaction mass is filtered off and the filter residue washed with 45 ml of isopropanol and again filtered.300 ml water are added to the humid filter residue and the mixture is stirred for 3 hours at 353 K. Then the temperature is decreased to 295 K and the mixture filtered off. The filter residue is washed with 100 ml water, filtered and dried in vacuum to obtain 16 g of compound of formula (101).

^{1}H-NMR Data in deuterated methanol (128 scans)/ 360MHz:

7.924	d	7.3	3.95	phenylen
7.5109	S		3.82	imidazol
6.857	d	7.8	3.96	phenylen
4.038	s		12.06	dimethyl
3.595	t		3.982	methylen
2.925	t		4.00	methylen

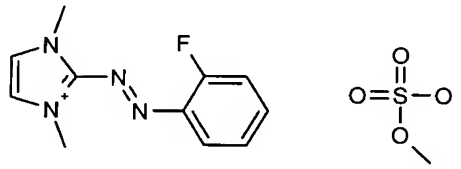
Example A2

(102) 

12.4 g 2-fluoroanilin are added to a stirred solution of 25 ml water and 25 ml of 32% hydrochloric acid at 295 K. The reaction mixture is cooled to 273 K and 19 ml 36% sodium nitrite solution are dropped at such a rate that the temperature of the mixture is maintained in the range of 273 to 276 K. After the addition of the sodium nitrite solution the mixture is stirred for one hour. If no excess of nitrite is detected during one hour (detection by using a potassium iodide/starch paper) further amounts of sodium nitrite solution are added. Then the remaining excess of nitrite is destroyed with sulfamic acid. The obtained diazo solution is dropped to a 273 K cold solution of 7.4 g imidazole in 30 ml water, whereby the pH of the solution is maintained in the range of pH 10 to 11 by adding 36% sodium hydroxide solution. After completing the diazo addition the obtained suspension is warmed up to 295 K and the pH is adjusted to 10.5 with 36% sodium hydroxide solution. After stirring for one hour at this pH and temperature the suspension is filtered off and then washed twice with 50 ml water to

obtain 55 g of the humid product, which is suspended in 500 ml water. 0.3 mol dimethyl sulfate and sodium hydroxide are simoultaniously added for maintaining the pH in the range of 10-10.3 and the temperature at 298-303K. The reaction mixture is hold for one hour. Then the water is evaporated.

About 40 g humid solid, which gives 27 g of dryed product of the formula

(102a) 

is obtained

The product is characterized by ^{1}H-NMR Data in deuterated methanol (128 scans)/ 360MHz:

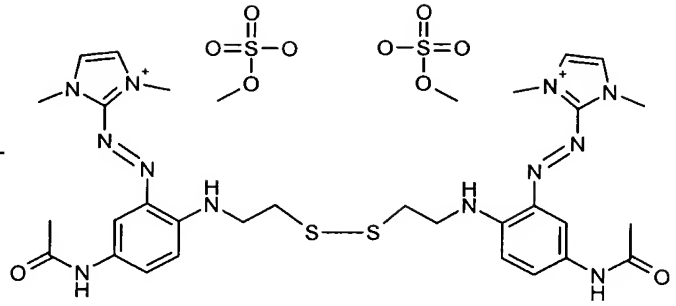
8.002	ddd	J = 7.6;J=7.5; j =1.4	1.029	
7.893	s		2.00	imidazol
7.812	m	J = 8.6, J = 6.7, J = 1.4	0.99	
7.505	ddd	J = 8.6	1.06	
7.436	t		0.949	
4.211	s		5.78	dimethyl of imidazol
3.69	s		4.01	methy of monomethylsulfate

11g cisteamin chlorohydrate are added to 27g of compound of formula (102a) in 20 g triethylamine and 120g isopropanol under nitrogen atmosphere at 293 K, .The temperature is raised to 333 K. The reaction mixture is stirred for 28 hours at this temperature. Then the reaction mass is stirred for 4 hours while the temperature is decreased to 295 K. The reaction mass is filtered off and the filter residue washed with 45 ml isopropanol and dried in vacuum to obtain 17.6 g of product f formula (102).

The product is characterized by ^{1}H-NMR Data in deuterated methanol (128 scans)/ 360MHz:

7.78	dd	J = 8.6; J =1.4	2.07	
7.620	s		4.00	imidazol
7.498	m	J = 8.6; J = 6.7 J = 1.4	1.968	
7.083	d	J = 8.6	1.875	
6.831	m		1.938	
4.057	s		12.08	dimethyl of dmidazol
3.846	t	6	3.75	methylene
3.69	s		4.01	methy of monomethylsulfate
3.109	t	6	3.95	methylene

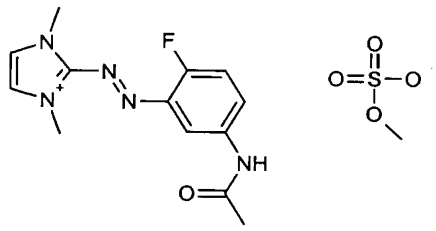
Example A3

(103)_ 

100 g 4-fluoro-3nitroanilin are added to a stirred mass of 80 g methanol and heated to 333 K. 0.1 ml sulfuric acid and 90 ml of acetic anhydride are added during 15 minutes. Heating and boiling are continued for 15 minutes. Then the reaction mixture is cooled slowly to 273 K with stirring. At the final temperature stirring is continued for 30 minutes, then the suspension is filtered off, washed with cold methanol, dryed in the vacuum dryer getting 114 g acetyl derivative which is worked up further. The acetyl derivative is solved in 520 ml ethanol and continuously added to 130 g iron in 35 ml concentrated hydrochloric acid and 220 ml water at 363K during 1 hour. The temperature drops to 353 K. The reaction mixture is stirred for further 3 hours. The hot mass is separated through filtration the residue washed with 100 ml ethanol. The filtrate and wash solution are cooled to 380 K with mixing, when cristallization of the product takes place. The product is separated by filtration, washed with cold ethanol and dryed in a vacuum dryer.

The dried material is dissolved in 132 ml water and 110 ml of 32% hydrochloric acid at 295 K. The reaction mixture is cooled to 273 K and 86.4 g 36% sodium nitrite solution are dropped at such a rate that the temperature of the mixture is maintained in the range of 273 to 276 K. The mixture is further stirred for one hour. If no excess of nitrite is detected during one hour (detection by using a potassium iodide/starch paper) further amounts of sodium nitrite solution are added. After this one hour the remaining excess of nitrite is destroyed with sulfamic acid. Then the obtained diazo solution is dropped to a 273 K cold solution of 33.4 g imidazole in 130 ml water, whereby the pH of the solution is maintained in the range of pH 10 to 11 by adding 36% of a sodium hydroxide solution. After completing the diazo addition, the obtained suspension is warmed up to 295 K and the pH is adjusted to 10.5 with 36% sodium hydroxide solution. After stirring for one hour at this pH and temperature the suspension is filtered off and then washed twice with 100 ml water to obtain 200 g of the humid product. The filtercake from the previouse step is suspended in water and 3 weight equivalents dimethylsulfate and sodium hydroxide are simultaniously added for maintaining the pH in the

range of 10-10.3 and the temperature at 300 K. Then the reaction mixture is hold for one more hour to finish the hydrolysis of excess of dimethylsulfate. Then the suspension is separated by filtration. About 240 g of a humid solid which gives 140 g dryed product of formula

(103a) 

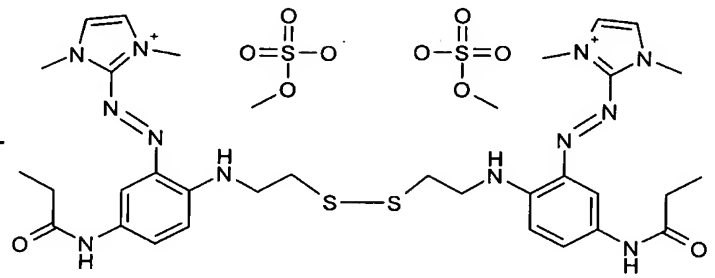
Is obtained.

38.8 g of the product of formula (103a) are added to a stirred mixture of 10.6 g of cisteamin chlorohydrate in 15 g triethylamine and 70g acetonitrile under nitrogen atmosphere at 293 K. The temperature is maintained at 273 K. The reaction mixture is stirred for 20 hours at this temperature. The reaction mass is filtered off and the filter residue washed with 45 ml of aceto-nitrile and dried in vacuum to obtain 42 g of product of formula (103).

The product is characterized by ^{1}H-NMR Data in deuterated methanol (128 scans)/ 360MHz:

8.11	d, J = 1.7	2,00	orto
7.6	d,d, J = 8.6;J =1.4	6,06	para
7.57	s		imidazol
7.00	d, J = 9.5	2,04	meta
4.03	s	12,22	methyl
3.860	t	3,89	methylene
3.69	s	6,44	methylsulfate
3.1o9	t	4,28	methylene
2.14	s	6.22	acetyl

Example A4

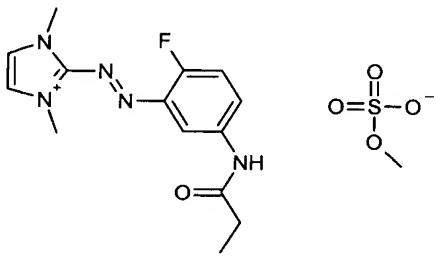
(104)_ 

100 g 4-fluoro-3nitro-anilin is added to a stirred mass of 80 g methanol, heated to 333 K, 0.1 ml sulfuric acid added, and then 90 ml of propionic anhydride during 15 minutes. Then

heating and boiling is continued for 15 minutes. Then the reaction mixture is cooled slowly to 273 K with stirring. At the final temperature stirring is continued for 30 minutes, then the suspension is filtered, washed with cold methanol, dryed in the vacuum dryer getting 114 g acetyl derivative which is worked up further. Then, the acetyl derivative is solved in 520 ml ethanol and continuously added to 130 g iron in 35 ml concentrated chlorhidric acid and 220 ml water at 363K during 1 hour. The temperature drops to 353 K. The reaction mixture is stirred for further 3 hours. The hot mass is separated through filtration, the residuu washed with 100 ml ethanol. The filtrate and wash solution is cooled to 380 K with mixing, when cristallization of the product takes place. The product is separated by filtration, washed with cold ethanol and dryed in a vacuum dryer.

The dried material is dissolved in 132 ml water and 110 ml of 32% hydrochloric acid at 295 K. Then the reaction mixture is cooled to 273 K and 86.4 g 36% sodium nitrite solution is dropped at such a rate that the temperature of the mixture is maintained in the range of 273 to 276 K. After the addition of the sodium nitrite solution, the mixture is stirred for one hour. If no excess of nitrite is detected during one hour (detection by using a potassium iodide/starch paper), further amounts of sodium nitrite solution is added. After this one hour the remaining excess of nitrite is destroyed with sulfamic acid. Then, the obtained diazo solution is dropped to a 273 K cold solution of 33.4 g imidazole in 130 ml water, whereby the pH of the solution is maintained in the range of pH 10 to 11 by adding 36% sodium hydroxide solution. After completing the diazo addition, the obtained suspension is warmed up to 295 K, the pH is adjusted to 10.5 with 36% sodium hydroxide solution. After one hour stirring at this pH and temperature, the suspension is filtrated and then washed twice with 100 ml water to obtain 200 g of the humid product

Then, the filtercake from the previouse step is suspended in water and 3 weight equivalents dimethylsulphate and sodium hydroxide simoultaniously added for maintaining the pH in the range of 10-10.3 and the temperature at 300 K. Then, the reaction mixture is hold for one more hour, to finish the hydrolysis of excess of dimethylsulphate. Then, the suspension is separated by filtration. About 240 g humid solid, which gives 140 g dryed product of formula

(104a) 

Characterizatiin by ^{1}H-NMR Data in deuterated methanol (128 scans)/ 360MHz

			Residue of compound
8.415	d, J = 2.7; 6.6	0.95	ortho coupling
7.889	s	2.00	imidazol
7.820	d,d,d;	0.98	para coupling
7.468	d,d J = 9.5: 9.5	1.04	meta coupling
4.203	s	6.22	methyl
3.69	s	3.00	methylsulfat
2.175	q	2.22	propionyl
1.20	t	3.28	propionyl

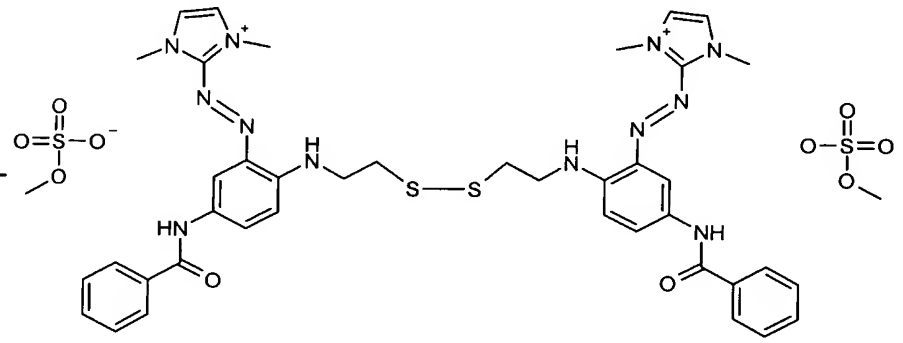
38.8 g of the product of formula (104a) are added under nitrogen atmosphere at 293 K to a stirred mixture of 10.6 g of cisteamin chlorohydrate in 15 g triethylamine and 70g acetonitrile. The temperature is maintained at 273 K. The reaction mixture is stirred for 20 hours at this temperature. The reaction mass is filtered off and the filter residue is washed with 45 ml of acetonitrile and dried in vacuum to obtain 32.6 g of product of formula (104).

Characterization by ^{1}H-NMR Data in deuterated methanol (128 scans)/ 360MHz

			Residue of compound (104)
8.11	d, J = 1.7	2.00	ortho coupling
7.6 overlaid	d,d, J = 8.6; J =1.4	6.06	para coupling
7.57	s		imidazol
7.00	d, j = 9.5	2.04	meta coupling
4.03	s	12.22	methyl
3.860	t	3.89	methylene
3.69	s	6.44	methylsulfate
3.1o9	t	4.28	methylene
2.14	q	4.22	propionyl
1.20	t	6.27	propionyl

Example A5

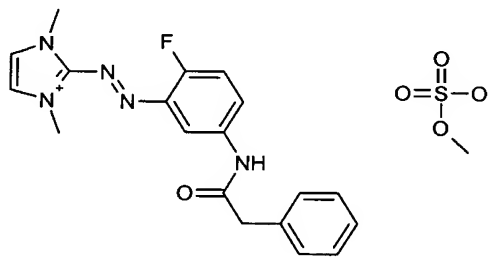
(105)



100 g 4-fluoro-3nitro-anilin are added to a stirred mass of 80 g methanol and heated to 333 K. 0.1 ml sulfuric acid and 90 ml of benzoyl chloride are added during 15 minutes. Heating

and boiling is continued for 15 minutes. The reaction mixture is cooled slowly to 273 K with stirring andcontinued for 30 minutes. The suspension is filtered off, washed with cold methanol, dryed in the vacuum dryer getting 114 g acetyl derivative which is worked up further. The acetyl derivative is dissolved in 520 ml ethanol and continuously added to 130 g iron in 35 ml concentrated chlorhidric acid and 220 ml water at 363K during 1 hour. The temperature drops to 353 K. The reaction mixture is stirred for further 3 hours. The hot mass is separated through filtration, the residue washed with 100 ml ethanol. The filtrate and wash solution are cooled to 380 K with mixing when cristallization of the product takes place. The product is separated by filtration, washed with cold ethanol and dryed in a vacuum dryer. The dried material is dissolved in 132 ml water and 110 ml of 32% hydrochloric acid at 295 K. Then the reaction mixture is cooled to 273 K and 86.4 g of a 36% sodium nitrite solution are dropped at such a rate that the temperature of the mixture is maintained in the range of 273 to 276 K. After the addition of the sodium nitrite solution the mixture is stirred for one hour. If no excess of nitrite is detected during one hour (detection by using a potassium iodide/starch paper) further amounts of sodium nitrite solution are added. The remaining excess of nitrite is destroyed with sulfamic acid. Then the obtained diazo solution is dropped to a 273 K cold solution of 33.4 g imidazole in 130 ml water, whereby the pH of the solution is maintained in the range of pH 10 to 11 by adding 36% of a sodium hydroxide solution. After completion of thethe diazo addition the obtained suspension is warmed up to 295 K, the pH adjusted to 10.5 with 36% sodium hydroxide solution. After stirring for one hour at this pH and temperature the suspension is filtered off and then washed twice with 100 ml water to obtain 200 g of the humid product Then the filtercake from the previouse step is suspended in water and 3 weight equivalents dimethylsulfate and sodium hydroxide simoultaniously added for maintaining the pH in the range of 10-10.3 and the temperature at 300 K. Then the reaction mixture is hold for one more hour to finish the hydrolysis of excess of dimethylsulfate. Then, the suspension is separated by filtration.

About 240 g of a humid solid, which gives 140 g dry product of the following formula

(105a) 

is obtained

Characterizeation by ^{1}H-NMR Data in deuterated methanol (128 scans)/ 360MHz

			Residue of compound
8.415	D, j = 2.7; 6.6	0.95	ortho coupling
7.889	s	2.00	Imidazol
7.820	d,d,d;	0.98	para coupling
7.468	D,d j = 9.5: 9.5	1.04	meta coupling
4.203	s	6.22	methyl
3.69	s	3.oo	methylsulfat

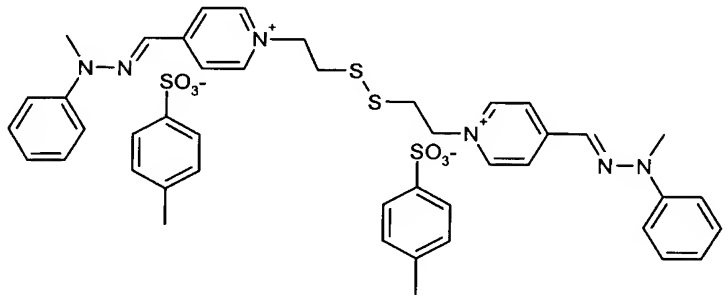
48 g of the compound of formula (105a) are added to a stirred mixture of 11.6 g of cisteamin chlorohydrate in 15 g triethylamin and 70g acetonitrile under nitrogen atmosphere at 293 K. Then the temperature is maintained at 273 K. The reaction mixture is stirred for 20 hours at this temperature. The reaction mass is filtered off and the filter residue is washed with 45 ml acetonitrile and dried in vacuum to obtain 42.6 g of the compound of formula (105).

Characterization by ^{1}H-NMR Data in deuterated methanol (128 scans)/ 360MHz:

			Residue of compound
8.11	d, j = 1.7	2.00	ortho coupling
7.6 overlaid	d,d, J = 8.6; j =1.4	6.06	para coupling
7.57	S		Imidazol coupling
7.00	d, j = 9.5	2.04	meta coupling
4.03	s	12.22	methyl
3.860	t	3.89	methylene
3.69	s	6.44	methylsulfat
3.1o9	t	4.28	methylene

Example A6

(106)



1.Formation of the Hydrazone: 14 g sulfuric acid are added to 42 g of water and cooled to 293K. 24 g of N-methyl-phenyl hydrazine (100%) are added with stirring. 24.5 g of 4-pyridine-aldehyde are dropped in during 15 minutes and stirring is continued for 1 hour. The pH is raised to 2.2 by adding a solution of 36% sodium hydroxide in water. 2.7 g sodium chloride are added at the 333K. Stirring is continued at this temperature for one hour. The slurry is

separated by filtration; the filter cake is dried at 343K in vacuum to yield 42 g of an orange powder.

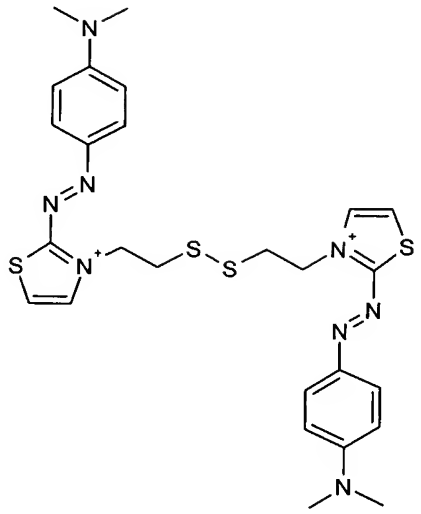
2. Alkylating agent: A mixture of 15.4 g of 2.2-dithiodiethanol in 100 ml chloroform and 24.1 g pyridine are cooled with stirring at 273K and then 41.0 g of tosyl chloride are added in small amounts, maintaining the temperature.
After completion of the addition the mixture is left over night in the refrigerator. The reaction mixture is mixed with a water/hydrochloric acid/ice slurry. The phases are separated, washed with water and dried. The obtained solution of toluenesulfonate diester is used in the 3. step.

3.Alkylation: The foregoing hydrazone is dissolved by stirring with the equivalent amount of diester solution. Temperature is raised to 334K which is maintainedduring the following 48 hours. Crystals separated in the slurry are filtred off. The product is washed with 50 ml chloroform and dried in vacuum to obtain 59 g of an orange solid product. The product is recristallized twice from methanol.

Characterization by ^{1}H-NMR data in deuterated methanol (32 scans)/ 360MHz:

				Residues of the compound
8.632	d	6.8	4.00	pyridinyl
8.070	d	6.7	3.98	pyridinyl
7.701	d	7.0	3.74	tosylate
7.648	s		2.04	hydrazon
7.528	d	6.1	3.967	phenyl
7.410	t	6.1	4.025	phenyl
7.195	t	6.6	3.846	tosylate
7.148	t	6.4	2.05	phenyl
4.78	t	6.77	4.00	ethylene
3.625	s		6.05	mehydrazon
3.385	t	6.55	4.087	ethylene
2.326	s		5.90	tosylate

Example A7

(107) 

1. Monoazo: 50.0 of g 2-amino-thiazol are added to a stirred solution of 135 ml 60% sulfuric acid at 293-310 K. Then, the reaction mixture is cooled to 273 K and 81 ml of a 40% nitrosilsulfuric acid are dropped at such a rate that the temperature of the mixture is maintained in the range of 273 to 276 K by cooling. After the addition the mixture is stirred for four hours. The solution is dropped to a well-stirred water ice mixture (400 g) containing 2,5 g amidosulfuric acid. To the obtained diazo solution (at 273 K ice added if need) 60,5 g dimethylaniline are dropped. Then the pH of the solution is raised to the range of 5 to 6 by adding 36% sodium hydroxide solution. After one hour stirring at this pH and temperature the suspension is filtered off and then washed twice with 50 ml water to obtain 155 g of the humid product. After drying 100 monoazo dye is obtained.

2. Alkylating agent: A mixture of 15.4 g of 2,2-dithiodiethanol in 100 ml chloroform and 24,1 g pyridine are cooled with stirring to 273 K and then 41.0 g of tosyl chloride are added in small amounts maintaining the temperature.
After completion of the addition the mixture is left over night in the refrigerator. The reaction mixture is mixed with a water/hydrochloric acid/ice slurry, the phases are separated, washed with water and dried. The obtained solution of toluenesulfonate diester is used in the following step

3.Alkylation: The foregoing monoazo is dissolved by stirring into the diester solution. Temperature is raised to 333K. The temperature is maintained at 333K during the following

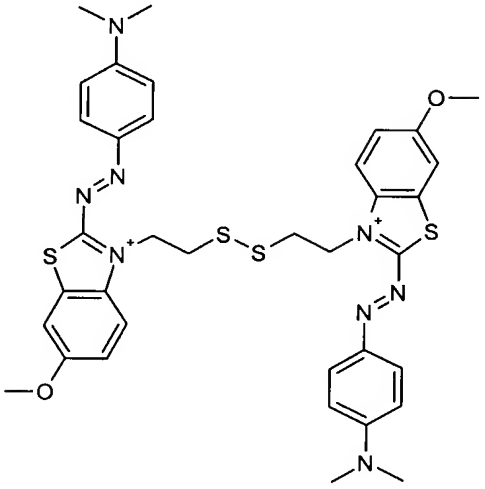
60 hours. Crystals separated in the slurry are filtered off. The product is washed with 50 ml of chloroform and dried in vacuum to obtain 59 g of a dark violett solid product.
The product is recristallized twice from methanol.

Characterization by ^{1}H-NMR Data in deuterated methanol (128 scans)/ 360MHz:

				Residues of the compound
8.095	d	J = 8.6;	2.07	
7.867	d	J=4.2	2.00	thiazol
7.696	d	overlaid	6	phenylene
7.470	d	J = 4.3	1.968	thiazol
7.217	d	J = 8.6	4.00	tosyl
7.083	d	J = 8.6	3.97	phenylene
4.856	t	5.6	4.08	methylene
3.419	s		12	methyl
3.139	t	5.6	4.01	methylen
2.309	s		6.00	Methyl

Example A8:

(108)



Monoazo synthesis

90.0 g 2-amino-6-methoxy-benzothiazol are added to a stirred solution of 135 ml 60% sulfuric acid at 293 K. The reaction mixture is cooled to 273 K and 81 ml of a 40% nitrosilsulfuric acid are dropped at such a rate that the temperature of the mixture is maintained in the range of 273 to 276 K with cooling and stirred for four hours. The solution is dropped to a well-stirred water ice mixture (400 g) containing 2.5 g amidosulfuric acid. 60,5 g dimethylaniline are dropped to the obtained diazo solution (at 273 K ice added if need). The pH of the solution is adjusted between 5 and 6 by adding 36% sodium hydroxide solution. After stirring for one hour at this pH and temperature the suspension is filtered off and

washed twice with 50 ml water to obtain 255 g of the humid product. After drying 151 monoazo dye is obtained.

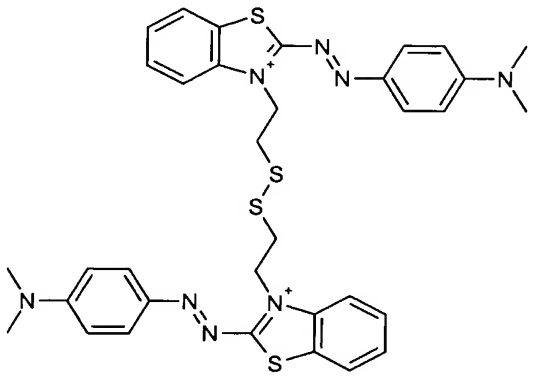
2. Alkylating agent: A mixture of 21.4 g of 2.2-dithiodiethanol in 100 ml chloroform and 24.1 g pyridine are cooled with stirring to 273K and then 41.0 g of mesyl anhydride are added in small amounts under constant temperature.
After completion of the addition the mixture is left over night in the refrigerator to finish the reaction. The reaction mixture is mixed with a water/hydrochloric acid/ice slurry, the phases are separated, washed with water and dried. The obtained solution of methanesulfonate diester is used in the following step

3.Alkylation: Two equivalents of the foregoing monoazo are dissolved by stirring into the diester solution. Temperature was raised to 334K. The temperature was maintained at 334K during the following 80 hours. Crystals separated in the slurry are filtered off. The product is washed with 50 ml of chloroform and dried in vacuum to obtain 80 g of a dark violett solid product. The product is recristallized twice from methanol.
Characterization by ^{1}H-NMR in deuterated methanol (128 scans)/ 360MHz:

				Residues of compound
7.924	d	7.3	3.95	phenylene
7.5109	s		3.82	imidazol
6.857	d	7.8	3.96	phenylene
4.038	s		12.06	dimethyl
3.595	t		3.982	methylene
2.925	t		4.00	methylene

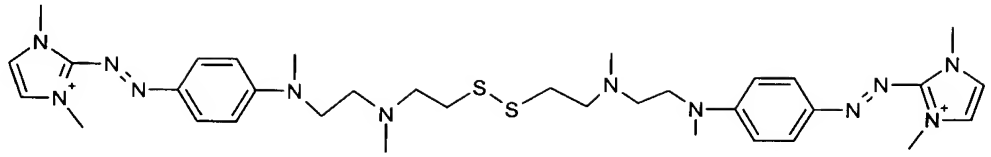
Example A9

(109)



Same preparation process as described in example A8, but with the difference that 2-amino-benzothiazol instead of 2-amino-6-methoxy-benzothiazol is used.

Example A10:

(110) 

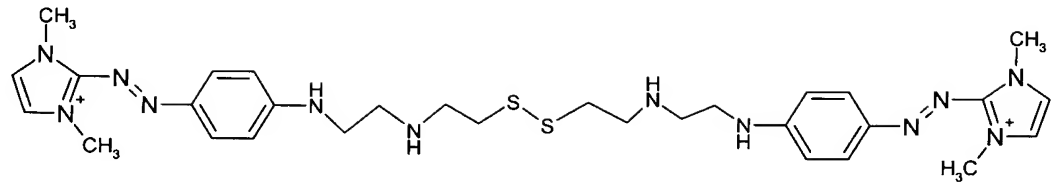
19.9 g of N,N'-dimethyl-ethylendiamine are added with stirring to 120g acetonitrile and compound of the formula of formula (101a) at 293 K under nitrogen atmosphere.
The temperature is raised to 333 K while the viscosity of the reaction mixture decreases. The reaction mixture is stirred at this temperature during 25 hours. Then the reaction mass is stirred for 4 hours while the temperature is decreased to 295 K. The reaction mass is filtered off and the filter residue is washed with 45 ml of acetonitrile. Then the material is dried in vacuum to obtain 16 g of product.

2. Alkylating agent: A mixture of 15.4 g of 2.2-dithiodiethanol in 100 ml chloroform and 24.1 g pyridine are cooled with stirring to 273K and then 41.0 g of tosyl chloride are added in small amounts under constant temperature.
After completion of the addition the mixture is left over night in the refrigerator. The reaction mixture is mixed with a water/hydrochloric acid/ice slurry, the phases are separated, washed with water and dried. The obtained solution of methane-benzene-sulfonate diester is used in the following step.

3.Alkylation: Stirring into the diester solution in chloroform dissolves two equivalents of the foregoing monoazo. Temperature is raised to 333K. The temperature is maintained at 333K during the following 20 hours. Crystals separated in the slurry are filtrated. The product is washed with 50 ml of chloroform and dried in vacuum to obtain 80 g of a dark solid product. The product is recristallized twice from methanol.

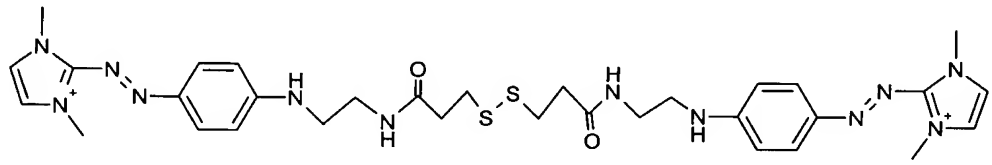
				Residue of compound
7.924	d	7.3	3.95	phenylen
7.5109	s		3.82	imidazol
6.857	d	7.8	3.96	phenylen
4.038	s		12.06	dimethyl
3.595	t		3.982	methylen
2.925	t		4.00	methylen

Example A11

(111) 

Same preparation process as described in example A10, but with the difference that ethylendiamine is used instead of N,N'-dimethyl-ethylendiamine.

Example A12

(112) 

1. 16.9 g of ethylenediamine are added to the compound of the formula (101a) (prepared in Example A1) and120g isopropanol at 293 K under nitrogen atmosphere under stirring. The temperature is raised to 333 K while the viscosity of the reaction mixture decreases. The reaction mixture is stirred at this temperature during 25 hours. Then the reaction mass is stirred for 4 hours while the temperature is decreased to 295 K. The reaction mass is filtered off and the filter residue is washed with 45 ml of isopropanol. Then the filter residue is dried in vacuum to obtain 16 g of the product.

2. Acylating agent: A mixture of 15.4 g of 2,2-dithiodipropionic acid and then 41.0 g of thionyl chloride is warmed to 333 K for 2 hours under constant temperature.

After completion of the addition the mixture is distilled under vacuum .

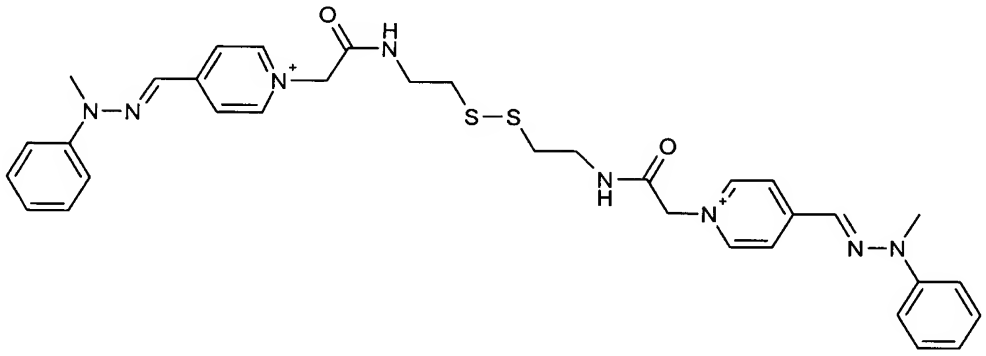
3.Alcylation: Two equivalents of the foregoing monoazo are dissolved by stirring into the acid chloride solution in chloroform. The temperature is raised to 333K and maintained during the following 48 hours. Crystals separated in the slurry are filtrated. The product is washed with 50 ml of chloroform and dried in vacuum to obtain 80 g of a dark redish solid product which is recristallized twice from methanol.

^{1}H-NMR Data in deuterated methanol (128 scans)/ 360MHz

				Residues of compound
7.924	d	7.3	3.95	phenylen
7.5109	s		3.82	imidazol
6.857	d	7.8	3.96	phenylen
4.038	s		12.06	dimethyl
3.595	t		3.982	methylen

2.925	t		4.00	methylen

Example A13

(113) 

1.Formation of the Hydrazone: 14 g sulfuric acid are added to 42 g of water and cooled to 293K. 25 g of N-methyl-phenyl hydrazine (100%) are added with stirring. 24.0 g of 4-pyridine-aldehyde are dropped in during 15 minutes and stirring is continued for 1 hour. The pH is raised to 2.2 by adding a solution of 36% sodium hydroxide in water. 2.7 g sodium chloride are added at a temperature of 333K and stirred for one more hour at this temperature. The slurry is separated by filtration, the filter cake dried at 343K in vacuum to yield 43 g of an orange powder.

2. Alkylating agent: A solution of 22.5 g of cisteamine dichlorohydrate in water and 31.4 g bromoacetic chloride are cooled with stirring to 273K and then the pH is kept constant by adding NaOH solution in small amounts under constant temperature.

After completion of the addition the mixture is left over night in the refrigerator. The mixture has two phases, which are separated, washed with water and dried.

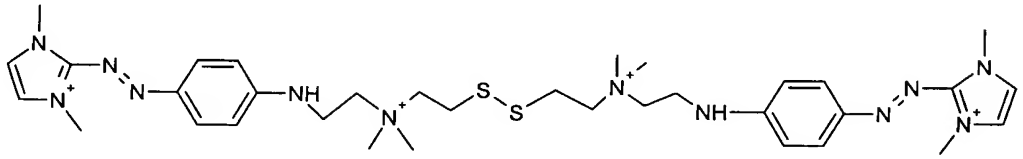
3. Alkylation: The foregoing hydrazone is dissolved in methanol by stirring with the dibromide solution. The temperature is raised to 60°C and maintained at 60°C during the following 24 hours. The crystals separated in the slurry are filtrated. The product is washed with 50 ml of methanol and dried in vacuum to obtain 49 g of an orange solid product. The product is recristallized twice from methanol.

Characterization by ^{1}H-NMR data in deuterated methanol (32 scans)/ 360MHz:

				Residues of the compound
8.442	d	6.8	4.00	pyridinyl
8.007	d	6.7	3.935	pyridinyl
7.517	s		2.04	hydrazon
7.4	m		8.08	phenyl
7.162	t	6.4	1.982	phenyl
5.235	s		3.648	ethylene

				Residues of the compound
3.625	t	6.75	3.05	ethylene
3.489	s		6.23	methyl
2.947	t	6.55	4.087	ethylene

Example A 14:

(114) 

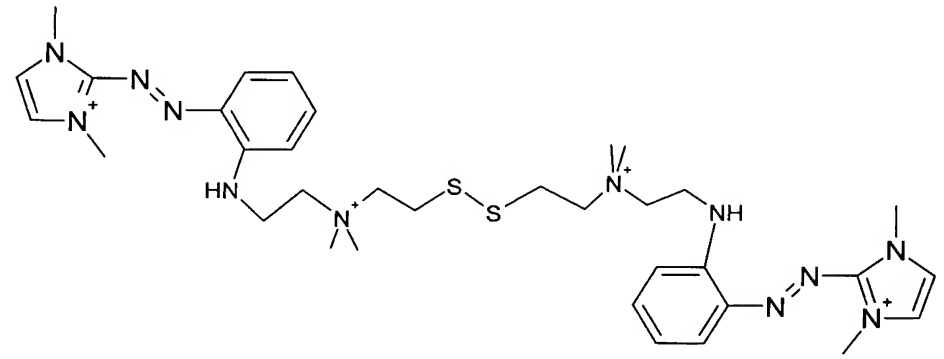
1. 9.9 g of N,N-dimethyl-ethylendiamine are added to 120g acetonitrile and to the compound of the formula (101a) (prepared in example A1) at 293 K under nitrogen atmosphere with stirring. The temperature is raised to 333 K while the viscosity of the reaction mixture decreases. The reaction mixture is stirred at this temperature during 25 hours.
The reaction mass is stirred for 4 hours while the temperature is decreased to 295 K. The reaction mass is filtered off and the filter residue washed with 45 ml of acetonitrile. Then the material is dried in vacuum to obtain 16 g of product.
2. Alkylating agent:A mixture of 15.4 g of 2.2-dithiodiethanol in 100 ml chloroform and 24,1 g pyridine is cooled with stirring to 273K and then 41.0 g of tosyl chloride are added in small amounts under constant temperature. After completion of the addition the mixture is left over night in the refrigerator. The reaction mixture is mixed with a water/chlorhidric acid/ice slurry, the phases are separated, washed with water and dried. The obtained solution of methane-benzene-sulfonate diester is used in the following step
3.Alkylation: Stirring into the diester solution in chloroform dissolves two equivalents of the foregoing monoazo. The temperature is raised to 333K and maintained at 333K during the following 20 hours. Crystals separated in the slurry are filtrated. The product is washed with 50 ml of chloroform and dried in vacuum to obtain 80 g of a dark solid product, which is recristallized twice from methanol.

				Residue of compound
7.966	d	7.3	3.95	phenylene
7,718	d	8	4,04	tosylate
7.564	s		3.82	imidazol
7,226	d	8	4,05	tosylate
6.927	d	7.8	3.96	phenylene
4.050	s		12.06	dimethyl
3,90	m		4,1	methylene
3,76	m		4,	methylene
3.595	t		3.982	methylene

3,31	s		12	methyl
2.925	t		4.00	methylene
2,32	s			methyl

Example 15:

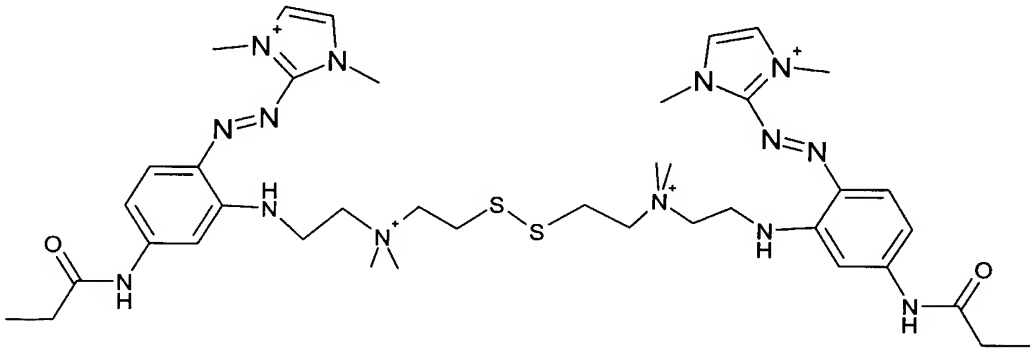
(115)



The compound of formula (102a) (prepared in example 2) is reacted with N,N-dimethyl-ethylenediamine according to the procedure as described in Example A14. The same alkylating agent is used to give the compound of formula (115).

Example A 16:

(116)



The compound of formula (104a) (prepared in example A 4) is reacted with N,N-dimethyl-ethylendiamine according to the method as described in Example A14.
The same alkylating agent is used and the compound of formula (116) is obtained.

Example B/ Application Examples:

The washing fastness of the dyed hair is analyzed by the Grey scale according to Industrial organic pigments by Herbst&Hunger, 2nd ed. engl. S. 61) Nr 10: DIN 54 001-8-1982, „Herstellung und Bewertung der Aenderung der Farbe", ISO 105-A02-1993.

In the following application examples compositions with definitions the below given are used:

Solution (1) (permanent lotion, pH 8.2): Aqua, Ammonium Thioglycolate, Ammonium Bicarbonate, Ethoxydiglycol, Hexylene Glycol, Thioglycolic Acid; Thiolactic Acid, PEG-60 Hydrogenated Castor Oil, Glycine, Etidronic Acid, Isoceteth-20, Polysilicone-9, Styrene/PVP Copolymer, Trideceth-12, Amodimethicone, Cetrimonium Chloride, Ammonium Hydroxide, Polyquaternium-6, Isopropyl Alcohol, Alcohol denat., Simethicone, Parfum

Solution (2) (permanent fixation, pH 3.9): Based on: Aqua, Hydrogen Peroxide, Propylene Glycol, Lauryldimonium Hydroxypropyl Hydrolyzed Wheat Protein, PEG-5 Cocamide, Sodium Cocoamphoacetate, Polyquaternium-35, Coco-Betaine, Acetaminophen, Phosphoric Acid, Sodium Chloride, Parfum

Solution (3) (dyeing solution): 0.1 % of the dye is dissolved in a 10 % solution of a non-ionic surfactant (Plantacare 200UP, Henkel) adjusted to pH 9.5 using citric acid or monoethanol-amine.

Solution (4) (permanent lotion, pH 8.7): Aqua, Thioglycolic Acid, Ammonium Bicarbonate, Ammonium Hydroxide, PEG-60 Hydrogenated Castor Oil, Sericin, Polyquaternium 22, Lauryldimmonium Hydroxypropyl Hydrolyzed Keratin, Hydroxyethyl Cetyldimonium Phosphate, Sodium Cocoamphopropionate, Parfum/Fragance, Styrene/PVP Copolymer, Pantasodium Pentetate, Ascorbic Acid, Benzyl Salicilate, Hydroxyisohexyl 3-Cyclohexene Carboxaldehyde, Hexyl Cinnamal, Butylphenyl Methylprpional, Linalool.

Solution (5) (permanent fixation, pH 2.9): Based on: Aqua, Hydrogen Peroxide, Hydroxycetyl Hydroxyethyl Dimonium Chloride, Tetrasodium Etidronate, PEG-40 hydrogenated Castor Oil, Salicylic Acid, Tetrasodium EDTA, Styrene/PVP Copolymer, Sericin, Parfum/Fragance, Phosphoric Acid.

Placebo colouring material:obtained by adding 11 ml ammonia solution (25% b.w.) at 343K to a composition consisiting of ammonium chloride 0.5% b.w., tetrasodium EDTA, 0.2% b.w., silica 0.1% b.w., water, add100% b.w..
Then, the obtained mixture is added to a composition consisting of cetearyl alcohol, 11% b.w., oleth-5, 5% b.w., oleic acid, 2.5% b.w., stearamide MEA, 2.5% b.w., cocoamide MEA, 2.5% b.w., propylene glycol 1.0% b.w..

Colouration composition of a placebo: The colouration composition of a placebo is obtained by adding 11 ml ammonia solution (25% b.w.) at 343K to a composition consisiting of

ammonium chloride 0.5% b.w., tetrasodium EDTA, 0.2% b.w., silica 0.1% b.w., water, add100% b.w. and 0.2% b.w. of a dyestuff.Then, the obtained mixture is added to a composition consisting of cetearyl alcohol, 11% b.w., oleth-5, 5% b.w., oleic acid, 2.5% b.w., stearamide MEA, 2.5% b.w., cocoamide MEA, 2.5% b.w., propylene glycol 1.0% b.w..

Example B1:

A tress of human hair, bleached white, is shampooed. Then, the towel dried hair tress is put on the glass plate. Solution (1) is applied to the wet hair tress. After 10 min the hair tress is rinsed under tap water and pressed out with a paper towel. Afterwards the tress is treated with a solution 3 containing the dye of formula (101) (Example A1) for 20 min and then rinsed with water. Then solution (2) is applied to the towel dried hair tress. After 10 minutes the hair tress is rinsed under tap water again and dried.
The tress is very intensive red with a very good wash fastness.

For comparison another tress of human hair, bleached white, is only treated with solution (3) containing the dye of formula (101) for 20 min and then rinsed with water and dried.
The tress shows a less intensive red and the wash fastness is much worse.

Example B2:

A tress of blonde undamaged human hair is shampooed. Then the towel dried hair tress is put on the glass plate.The solution (1) (permanent solution) is applied to the wet hair tress. After 10 min the hair tress is rinsed under tap water and pressed out with a paper towel. Afterwards the tress is treated with a solution 3 containing the dye from Example A2 for 20 min and then rinsed with water. Then solution (2) (permanent fixation) is applied to the towel dried hair tress. After 10 min. the hair tress is rinsed under tap water again and dried.
The tress is very intensive violet with a very good wash fastness.

For comparison another tress of blonde undamaged human hair is only treated with solution 3 containing the dye for 20 min and then rinsed with water and dried.
The tress is less intensive violet and the wash fastness is much worse.

Example B3:

0.1%, b.w. colouring material solution consisting of compound of formula (101) in plantaren solution (pH=9.5) is applied on the dry hair (two blond, two middle blond and two damaged

hair strands) and allowed to stand for 20 min. at room temperature. Then, the strands are rinsed under tap water and dried 12 hours.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	red	2-3
middelblond	red	3
damaged	red	3

Example B4:

0.1%, b.w. colouring material solution consisting of compound of formula (101) in plantaren solution (pH=9.5) is applied on shampooed hair (two blond, two middle blond and two damaged hair strands). Then the towel dry strands are put on a glasplate and treated with solution (1) (permanent lotion) and allowed to stand for 10 min. Then, the strands are rinsed under tap water and the towel dry strands are treated with a solution (2) (permanent fixation) and allowed to stand for 10 min. Then, the strands are rinsed under tap water and dried for 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	red	5
middelblond	red	5
brown	red	5
damaged	red	5

Example B5:

Same application as described in example B4, but with the difference that the compound of formula (101) is replaced by the compound of formula (102).

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	red	5
middelblond	red	5
brown	red	5
damaged	red	5

Example B6:

Solution (1) (permanent lotion) is applied on shampooed hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 5 min. Then the strands are rinsed under tap water and the towel dry strands are treated with a 0.1% b.w. colouring material solution consisting of compound of formula (101) in plantaren (pH=9.5) allowed to stand for 20 min and then rinsed. Then the towel dry strands are treated with a solution (2) (permanent

fixation) and allowed to stand for 10 min. Then the strands are rinsed under tap water and dried for 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	red	5
middelblond	red	5
brown	red	5
damaged	red	5

Example B7:

Solution (1) (permanent lotion) having a pH 8.2, which is mixed with a weight equivalent water to give a pH of 8.00 is applied on shampooed hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 10 min. Then the strands are rinsed under tap water and the towel dry strands are treated with a 0.1% b.w. colouring material solution consisting of the compound of formula (101) in plantaren (pH=9.5) and allowed to stand for 20 min and then rinsed. Then the towel dry strands are treated with solution (2) (permanent fixation) and allowed to stand for 10 min. Then the strands are rinsed under tap water and dried for 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	red	5
middelblond	red	5
Brown	red	5
damaged	red	4-5

Example B8:

Same application method as described in Example B7, but with the difference that the permanent wave solution allowed to stand for 5 min. instead of 10 min.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	red	4-5
middelblond	red	5
brown	red	5
damaged	red	4-5

Example B9:

Solution (1) (permanent lotion) with a pH 8.2 which is mixed with one weight equivalent water togive a pH of 8.00 is applied on shampooed hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 1 min. Then the strands are rinsed under tap

water and the towel dry strands are treated with a 0.1% b.w. colouring material solution consisting of the compound of formula (101) in plantaren (pH=9.5) allowed to stand for 10 minutes and then rinsed. Then the towel dry strands are treated with solution (2) (permanent fixation) and allowed to stand for 10 min. Then the strands are rinsed under tap water and dried for 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	red	4
middelblond	red	-
brown	red	-
damaged	red	4

Example B10:

A solution 1 (permanent lotion), having a pH 8.2, which is mixed with two weight equivalents water to give a pH of 8.0, is applied on shampooed hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 1 minutes.. Then the strands are rinsed under tap water and the towel dry strands are treated with a 0.1% b.w. colouring material solution consisting of compound of formula (101) in plantaren (pH=9.5) and allowed to stand for 20 min and then rinsed. Then the towel dry strands are treated with a solution 2 (permanent fixation) and allowed to stand for 10 min. Then, the strands are rinsed under tap water and dried for 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	red	4
middelblond	red	-
brown	red	-
damaged	red	4

Example B11:

A solution 1 (permanent lotion), having a pH 8.2, which is mixed with two weight equivalents water to give a pH of 8.08 is applied on shampooed hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 1 minute. Then the strands are rinsed under tap water and the towel dry strands are treated with a 0.1% b. w. colouring material solution consisting of the compound of formula (101) in plantaren (pH=9.5), allowed to stand for 10 min. and then rinsed. Then the towel dry strands are treated with a solution 2 (permanent fixation) and allowed to stand for 10 min. Then the strands are rinsed under tap water and dried for 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	red	4
middelblond	red	-
brown	red	-
damaged	red	3

Example B12:

A solution 1 (permanent lotion) having a pH 8.2 is applied on shampooed hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 10 min. Then, the strands are rinsed under tap water, and the towel dry strands are treated with a colouring material solution consisting of

a. compound of formula (101) according to example A1, 0.2%, b.w. solution in plantaren, and

b. a watery hydrogene peroxid solution, 6% b.w., which are mixed together in a weight ratio of 1:1, and then applied on the hair and allowed to stand for 30 min, and then, rinsed and then shampooed, and afterwards dried for 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	light red	2-3
middelblond	light red	2-3
brown	light red	4
damaged	light red	2

Application Example B13:

Solution 1 (permanent lotion; pH 8.2) is applied on shampooed hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 10 min. Then the strands are rinsed under tap water and the towel dry strands treated with a colouring material solution consisting of

a. compound of formula (101) according to example A1, 0.2%, b.w. solution in plantaren, and

b. placebo colouring material, which are mixed together in a weight ratio of 1:1, and then applied on the hair and allowed to stand for 30 min. and then rinsed.

Then the towel dry strands are treated with a solution (2) (permanent fixation), and allowed to stand for 10 min. Then the strands are rinsed under tap water and dried 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	red	5
middelblond	red	5
brown	red	5
damaged	red	5

Application Example B14:

Solution (1) (permanent lotion; pH 8.2) is applied on shampooed hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 10 min. Then the strands are rinsed under tap water and the towel dry strands are treated with a 0.1%, b.w. colouring material solution consisting of the compound of formula (101) insolution (2) (permanent fixation) and allowed to stand for 20 min. Then the strands are rinsed under tap water and dried 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	red	4
middelblond	red	4-5
brown	red	4-5
damaged	red	3

Application Example B15:

A composition consisting of

a. a solution 1 (permanent lotion), having a pH 8.2, and

b. a 0.2%, b.w. solution of compound of formula (101) in plantaren,

which are mixed together in a weight ratio of 1:1 is applied on shampooed hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 10 min. Then, the strands are rinsed under tap water. The towel dry strands are treated with a solution 2 (permanent fixation), and allowed to stand for 10 min. Then the strands are rinsed under tap water and dried 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	red	4-5
middelblond	red	5
brown	red	5
damaged	red	4-5

Example B16:

A composition consisting of

a. solution (1) (permanent lotion), having a pH 8.2, and

b. 0.1% b.w. solution of the compound of formula (101) in plantaren, which are mixed together in a weight ratio of 1:1, is applied on shampooed hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 20 min. Then, the strands are rinsed under tap water. The towel dry strands are treated with a solution (2) (permanent fixation), and allowed to stand for 10 min. Then the strands are rinsed under tap water and dried 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	red	4
middelblond	red	5
brown	red	5
damaged	red	3

Example B17:

A solution 1 (permanent lotion; pH 8.2) is applied on shampooed hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 20 min. Then the strands are rinsed under tap water and the towel dry strands are treated with a 0.1%, b.w. colouring material solution of compound of formula (101) in solution (2) (permanent fixation) and allowed to stand for 20 min. Then the strands are rinsed under tap water. The towel dry strands are treated with a composition consisting of a. a placebo colouring material and b. a aqueous hydrogen peroxide solution, 12 % b.w., and having a weight ratio of the placebo to the hydrogene peroxide solution of 1:1. Then the strands are allowed to stand for 30 min. The strands are rinsed under tap water, shampooed and dried 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	red	5
middelblond	red	5
brown	red	5
damaged	red	4-5

Example B18:

Solution (1) (permanent lotion; pH 8.2) is applied on shampooed hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 10 min. Then the strands are

rinsed under tap water and the towel dry strands are treated with a 0.1% b.w. colouring material solution of compound of formula (101) in solution (2) (permanent fixation) and allowed to stand for 20 min. Then the strands are rinsed under tap water. The towel dry strands are treated with a fixation composition consisting of a) ammonia and b) an aqueous hydrogen peroxide solution having a pH of 9.8. Then the strands are allowed to stand for 10 min. The strands are rinsed under tap water, shampooed and dried 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	red	5
middelblond	red	5
brown	red	5
damaged	red	4-5

Example B19:

A composition consisting of

a. a solution 1 (permanent lotion), having a pH 8.2, and

b. a 0.1%, b.w. solution of compound of formula (101) in plantaren which are mixed together in a weight ratio of 1:99 of component a) to b),

are applied on shampooed hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 20 min. Then the strands are rinsed under tap water. The towel dry strands are treated with a fixation composition consisting of a) ammonia and b) an aqueous hydrogen peroxide solution of pH of 9.8. Then the strands are allowed to stand for 10 min. The strands are rinsed under tap water shampooed and dried 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	red	4
middelblond	red	4-5
brown	red	5
damaged	red	3-4

Example B20:

A colouring material solution consisting of

a. 25 ml of a 0.1% b.w. solution of compound of formula (101), and

b. 25 ml of a 0.1% b.w. solution of compound of formula (106)

is applied on dry hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 30 min.

Washing fastness: 10 x washed with shampoo / Results	
Strand	Colour
blond	orange
middelblond	orange
brown	orange
damaged	orange

Example B21:

A solution 1 (permanent lotion; pH 8.2) is applied on shampooed hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 10 min. Then the strands are rinsed under tap water, and the towel dry strands are treated with a colouring material solution consisting of

a. 25 ml of a 0.1% b.w. solution of compound of formula (101) according to example A1 in plantaren, and
b. 25 ml of a 0.1% b.w. solution of compound of formula (106) according to example A6 in plantaren solution, allowed to stand for 20 min and then rinsed.

The towel dry strands are treated with a solution (2) (permanent fixation) and allowed to stand for 10 min. The strands are rinsed under tap water and dried 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	orange	5
middelblond	orange	5
brown	orange	5
damaged	orange	5

Example B22:

A composition consisting of

a. Solution 4 (permanent lotion) having a pH 8.7, is mixed with one equivalent water to access pH 8.6), and
b. 0.2%, b.w. solution of the compound of formula (101) in plantaren, which are mixed together in a weight ratio of 1:1,

are applied on shampooed hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 5 min. The strands are rinsed under tap water. The towel dry strands are treated with a solution (5) (permanent fixation) and allowed to stand for 10 min. The strands are rinsed under tap water and dried 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	red	5
middelblond	red	5
brown	red	5
damaged	red	5

Example B23:

A solution (1) (permanent lotion; pH 8.2) is applied on shampooed hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 10 min. The strands are rinsed under tap water and the towel dry strands treated with a colouring material solution consisting of

a. 0.2% b.w. solution of compound of formula (101) according to example A1, in plantaren, and

b. placebo colouring material, which are mixed together in a weight ratio of 1:1, and then applied on the hair and allowed to stand for 20 min and then rinsed.

The towel dry strands are treated with a solution 2 (permanent fixation) and allowed to stand for 10 min. The strands are rinsed under tap water and dried 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	red	5
middelblond	red	5
brown	red	5
damaged	red	5

Example B24:

Solution (1) (permanent lotion; pH 8.2) is applied on shampooed hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 10 min. Tthe strands are rinsed under tap water and the towel dry strands treated with a colouring material solution consisting of

a. 0.2% b.w. solution of compound of formula (101) according to example A1, in plantaren, and

b placebo colouring material, which are mixed together in aweight ratio of 1:1, and then, applied on the hair and allowed to stand for 10 min and then rinsed.

Then the towel dry strands are treated with solution (2) (permanent fixation) and allowed to stand for 10 min. Then the strands are rinsed under tap water and dried 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	Red	5
middelblond	Red	5
brown	Red	5
damaged	Red	4-5

Example B25:

Solution (1) (permanent lotion) is applied on shampooed hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 10 min. The strands are rinsed under tap water and the towel dry strands treated with a 0.1% b. w. colouring material solution of the compound of formula (101) in plantaren, allowed to stand for 20 min and then rinsed. The towel dry strands are treated with a solution 2 (permanent fixation) and allowed to stand for 10 min. The strands are rinsed under tap water and dried 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	red	5
middelblond	red	4
brown	red	5
damaged	red	4

Example B26:

A composition consisting of

a. a solution 1 (permanent lotion), having a pH 8.2, and

b. 0.1% b.w. solution of compound of formula (101) according to example A1 in plantaren,

which are mixed together in a weight ratio of 1:9 of component a) to b),

is applied on shampooed hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 20 min. Then, the strands are rinsed under tap water. The towel dry strands are treated with a solution 2 (permanent fixation), and allowed to stand for 10 min. Then, the strands are rinsed under tap water and dried 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	red	5
middelblond	red	4-5
brown	red	5
damaged	red	4

Example B27:

Solution (4) (permanent lotion; pH 8.7) is applied on shampooed hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 15 min. The strands are rinsed under tap water, and the towel dry strands treated with a colouring material solution consisting of

a 1.6 weight equivalents of a 0.1% b.w. solution of compound of formula (101) according to example A1 in plantaren solution,

b) 5 weight equivalents of of a 0.1% b.w. solution of compound of formula (106) according to example A6 in plantaren solution, and

c) 1.5 weight equivalents of a 0.1% b.w. solution of compound of formula (103) according to example A3 in plantaren solution,

and allowed to stand for 20 min. and then rinsed. The towel dry strands are treated with solution (5) (permanent fixation; pH 2.9) and allowed to stand for 10 min. The strands are rinsed under tap water and dried for 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	brown	4
middelblond	brown	4-5
damaged	brown	5
grey 70%	brown	5
grey 90%	brown	4-5

Example B28:

A colouring material solution consisting of

a 1.6 w. eq. of a 0.1% b.w. solution of the compound of formula (101) in plantaren, and

b. 5 w. eq. of of a 0.1% b.w. solution of compound of formula (106) in plantaren,

c. 1.5 w. eq. of a 0.1% b.w. solution of compound of formula (103) in plantaren solution,

is applied on dry hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 20 min.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	brown	2-3
middelblond	brown	2-3
damaged	brown	2
grey 70%	brown	2
grey 90%	brown	2

Example B29:

Hair (blond strand, damaged strand) is shampooed, rolled on curls windings and then treated with solution (4) (permanent lotion; pH 8.7) and then allowed to stand for 10 min. The hair is treated with a 0.1% b.w. solution of compound of formula (101) in plantaren and allowed to stand for 20 min at room temperature. The hair is rinsed under tap water, and the towel dry strands treated with a solution 5 (permanent fixation; pH 2.9) and allowed to stand for 5 min. Curl windings are removed and the hair is again treated with solution (5) (permanent fixation; pH 3.92) and allowed to stand for 5 min. The strands are rinsed under tap water and dried 12 hours at room temperature.

The strands are curled and red coloured.

Example B30:

Hair (blond strand, damaged strand) is shampooed and then rolled on curls windings and treated with solution (4) (permanent lotion; pH 8.7 which is diluted with 2 weight equivalents of water and then allowed to stand for 5 min. The hair is treated with 0.1% b.w. solution of compound of formula (101) in plantaren and allowed to stand for 20 min at room temperature. The hair is rinsed under tap water and the towel dry strands are treated with solution (5) (permanent fixation; pH 2.9) and allowed to stand for 10 min. The strands are rinsed under tap water and dried 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	red	4-5
middelblond	red	5
brown	red	5
damaged	red	4

Example B31:

Hair (blond strand, damaged strand) is shampooed and then rolled on curls windings and treated with solution (4) (permanent lotion; pH 8.7), which is diluted with 2 weight equivalents of water and allowed to stand for 10 min. The hair treated with 0.1% b.w. solution of the compound of formula (101) in plantaren and allowed to stand for 20 mın at room temperature. The hair is rinsed under tap water and the towel dry strands are treated with solution (5) (permanent fixation; pH 2.9) and allowed to stand for 10 min. The strands are rinsed under tap water and dried 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	red	4-5
middelblond	red	5
brown	red	5
damaged	red	4-5

Example B32:

A composition consisting of

a. a solution 1 (permanent lotion), having a pH 8.2, which are diluted with 4 weight equivalents of water, and

B. a 0.2% b.w. solution of compound of formula (101) in plantaren which are mixed together in a weight ratio of 1:2 of component a) to b),

is applied on shampooed hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 20 min. Then, the strands are rinsed under tap water. The towel dry strands are treated with a solution 2 (permanent fixation), and allowed to stand for 10 min. Then, the strands are rinsed under tap water and dried 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
strand	Colour	Washing fastness
blond	red	5
middelblond	red	5
brown	red	5
damaged	red	4-5

Example B33:

A composition consisting of 30 g of a 0.1% b. w. solution of the compound of formula (101) in plantaren having a pH of 6.12 is applied on shampooed hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 20 min. The strands are rinsed under tap water and dried 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
strand	Colour	Washing fastness
blond	red	2-4
middelblond	red	3-4
brown	red	5
damaged	red	3

Example B34:

A composition comprising

49.95 g of a 0.1%, b.w. solution of the compound of formula (101) in plantaren having a pH of 6.1, and

0.05g ammonium thioglycolate solution, and amonia and citronic acid for adjusting the pH to 8.0,

is applied on shampooed hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 20 min.. The strands are rinsed under tap water. The towel dry strands are treated with solution (2) (permanent fixation) and allowed to stand for 10 min. The strands are rinsed under tap water and dried 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	red	4-5
middelblond	red	5
brown	red	5
damaged	red	4-5
permanent waved	curled	

Example B35:

A composition comprising

49.75 g of a 0.1% b.w. solution (pH 6.12) of the compound of formula (101), and

0.25g ammonium thioglycolate solution, and amonia and citronic acid for adjusting the pH to 8.0,

is applied on shampooed hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 20 min.. The strands are rinsed under tap water. The towel dry strands are treated with a solution 2 (permanent fixation) and allowed to stand for 10 min. The strands are rinsed under tap water and dried 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	red	4-5
middelblond	red	5
brown	red	5
damaged	red	4-5
permanent waved	curled	

Example B36:

A composition comprising

49.5 g of a 0.1%, b.w. solution of compound of formula (101) (pH 6.12), and

0.55g ammonium thioglycolate solution, and ammonia and citronic acid for adjusting the pH to 8.0, is applied on shampooed hair (two blond, two middle blond and two damaged hair

strands) and allowed to stand for 20 min. The strands are rinsed under tap water. The towel dry strands are treated with solution (2) (permanent fixation) and allowed to stand for 10 min. The strands are rinsed under tap water and dried 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	red	4-5
middelblond	red	5
brown	red	5
damaged	red	4-5
permanent waved	curled	

Example B37:

10% b.w. of a solution of sodium sulfite in water having a pH of 8 (the pH is adjusted by ammonia and citric acid) is applied on shampooed hair (blond strand, damaged strand) and allowed to stand for 10 min. The hair is rinsed and treated then with 0.1% b.w. of a solution (pH 9.5) of the compound of formula (101) and allowed to stand for 20 min at room temperature. The hair is rinsed under tap water and the towel dry strands are treated with solution (5) (permanent fixation) having a pH 2.9 and allowed to stand for 10 min. The strands are rinsed under tap water and dried 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	red	4-5
middelblond	red	5
brown	red	5
damaged	red	4-5

Example B38:

A composition comprising

49.95 g of a 0.1% b.w. solution of the compound of formula (101) in plantaren (pH 6.12), and 0.05g of a 0.1% b.w. solution of sodium sulfite in water having a pH of 8 (the pH is adjusted by ammonia and citric acid),

is applied on shampooed hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 20 min. The hair is rinsed under tap water and the towel dry strands are treated with solution (5) (permanent fixation) having a pH 2.9 and allowed to stand for 10 min. The strands are rinsed under tap water and dried 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	red	4

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
middelblond	red	5
brown	red	4-5
damaged	red	4

Example B39:

A composition comprising

49g of a 0.1% b.w. solution of the compound of formula (101) in plantaren (pH 6.12), and

1g of a 2% b.w. solution of sodium sulfite in water having a pH of 8 (the pH is adjusted by ammonia and citric acid),

is applied on shampooed hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 20 min. The hair is rinsed under tap water and the towel dry strands are treated with a solution 2 (permanent fixation) and allowed to stand for 10 min. The strands are rinsed under tap water and dried 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	red	4-5
middelblond	red	5
brown	red	4-5
damaged	red	4
permanent waved	red and curled	

Example B40:

2% b.w. of a solution of sodium sulfite in water having a pH of 8 (the pH is adjusted by ammonia and citric acid) is applied on shampooed hair (blond strand, damaged strand) and then allowed to stand for 10 min. The hair is rinsed and treated then with 0.1% b.w. of a solution of the compound of formula (101) (pH 9.5) and allowed to stand for 20 min at room temperature. The hair is rinsed under tap water and the towel dry strands treated with solution (2) (permanent fixation) having a pH 3.92 and allowed to stand for 10 min. The strands are rinsed under tap water and dried 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	red	4-5
middelblond	red	4-5
brown	red	5
damaged	red	4

Example B41:

2% b.w. of a solution of ammonium thioglycolate in water (pH 8; adjusted with ammonia and citric acid) is applied on shampooed hair (blond strand, damaged strand) and then allowed to stand for 10 min. The hair is rinsed and treated with 0.1% b.w. of a solution of the compound of formula (101) according in plantaren (pH 9.5) and allowed to stand for 20 min at room temperature. The hair is rinsed under tap water and the towel dry strands are treated with solution (2) (permanent fixation) and allowed to stand for 10 min. The strands are rinsed under tap water and dried 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	red	4-5
middelblond	red	5
brown	red	5
damaged	red	3-4

Example B42:

2% b.w. of a solution of ammonium thiolactate in water (pH of 8; adjusted by ammonia and citric acid) is applied on shampooed hair (blond strand, damaged strand) and then allowed to stand for 10 min. The hair is rinsed and treated with 0.1% b.w. of a solution of the compound of formula (101) in plantaren (pH 9.5) and allowed to stand for 20 min at room temperature. The hair is rinsed under tap water and the towel dry strands treated with solution (2) (permanent fixation) and allowed to stand for 10 min. Then the strands are rinsed under tap water and dried 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	red	4-5
middelblond	red	4-55
brown	red	5
damaged	red	3-4

Example B43:

A composition comprising

49.95g of a 0.1% b.w. solution of the compound of formula (101) in plantaren (pH 6.12), and 0.05g of a 0.1% b.w. solution of ammonium thioglycolate in water having a pH of 6.1 (the pH is adjusted by ammonia and citric acid),

is applied on shampooed hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 20 min. Then the strands are rinsed under tap water and dried 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	red	3-4
middelblond	red	3-4
brown	red	5
damaged	red	3-4

Example B44:

A composition comprising

49.95g of a 0.1% b.w. solution of the compound of formula (101) (pH 6.12), and

0.05g of a 0.1% b.w. solution of ammonium thioglycolate in water having a (pH of 8.0; iadjusted by ammonia and citric acid),

is applied on shampooed hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 20 min. Then the strands are rinsed under tap water and dried for 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	red	3-4
middelblond	red	4
brown	red	5
damaged	red	3-4

Example B45:

A composition comprising

49.95g of a 0.1% b.w. solution of compound of formula (101) in plantaren (pH 6.12), and

0.05g of a 0.1% b.w. solution of ammonium thioglycolate in water (pH 8.0; adjusted by ammonia and citric acid),

is applied on shampooed hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 20 min. Then the hair is rinsed under tap water and the towel dry strands treated with a composition comprising component a) and b) in a weight ratio of 1:1, wherein a) is hydrogene peroxide, 6% b.w. solution in water, and b) is a colouration composition of a placebo and then are allowed to stand for 30 min. Then the strands are rinsed under tap water and dried 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	red	3-4
middelblond	red	4
brown	red	5
damaged	red	4

Example B46:

A solution of 0.1% b.w. of the compound of formula (101) in plantaren (pH 8; pH is adjusted with ethanol amin),

is applied on shampooed hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 20 min. Then the hair is rinsed under tap water and dried 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	red	4
middelblond	red	4-5
brown	red	5
damaged	red	3

Example B47:

A solution of 0.1% b.w. of the compound of formula (101) (pH 8; adjusted with ethanolamine) is applied on shampooed hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 20 min. The hair is rinsed under tap water and the towel dry strands treated with a composition comprising component a) and b) in a weight ratio of 1:1, wherein a) is hydrogen peroxide, 6% b.w. solution in water, and b) is a colouration composition of a placebo and are allowed to stand for 30 min. The strands are rinsed under tap water and dried for 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	red	3
middelblond	red	3
brown	red	5
damaged	red	2-3

Example B48:

A composition comprising

49.91g of a 0.1% b.w. solution of the compound of formula (101) in plantaren (pH 6.12), and

0.09g of a 0.1% b.w. solution of ammonium thiolactate in water (pH of 8.0; adjusted with ammonia and citric acid),
is applied on shampooed hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 20 min. Then the hair is rinsed under tap water and the towel dry strands treated with solution (2) (permanent fixation) and allowed to stand for 10 min. Then the strands are rinsed under tap water and dried for 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	red	4-5
middelblond	red	4-5
brown	red	5
damaged	red	4

Example B49:

A solution of 0.1% b.w. of the compound of formula (101) in plantaren (pH of 5.5; adjusted with ethanolamin) is applied on shampooed hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 20 min. Then the hair is rinsed under tap water and the towel dry strands are treated with a composition comprising component a) and b) in a weight ratio of 1:1, wherein a) is hydrogen peroxide, 6% b.w. solution in water, and b) is a colouration composition of a placebo and then allowed to stand for 30 min. The strands are rinsed under tap water and dried for 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	red	3
middelblond	red	3
brown	red	5
damaged	red	2-3

Example B50:

A composition comprising
49.57g of a 0.1% b.w. solution of the compound of formula (101), and
0.43g of a 0.1% b.w. solution of ammoniumthiolactate in water (pH 8.0; adjusted with ammonia and citric acid),
is applied on shampooed hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 20 min. Then the hair is rinsed under tap water and the towel dry strands are treated with solution (2) (permanent fixation) and allowed to stand for 10 min.. Then the strands are rinsed under tap water and dried for 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	red	4-5
middelblond	red	5
brown	red	5
damaged	red	4

Application Example B51:

A composition comprising

49.15g of a 0.1% b.w. solution of thecompound of formula (101) in plantaren (pH 6.12), and

0.85g of a 0.1% b.w. solution of ammoniumthiolactate in water (pH 8.0; adjusted with ammonia and citric acid),

is applied on shampooed hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 20 min.. The hair is rinsed under tap water and the towel dry strands treated with a solution (2) (permanent fixation) and allowed to stand for 10 min.. The strands are rinsed under tap water and dried 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	red	5
middelblond	red	5
brown	red	5
damaged	red	4-5

Example B52:

0.1% b.w. of a solution of ascobinic acid in water (pH 8; adjusted by ammonia and citric acid) is applied on shampooed hair (blond strand, damaged strand) and then allowed to stand for 10 min. Then, the hair is rinsed and treated then with 0.1% b.w. of a solution of compound of formula (101) according to example A1 in plantaren (with pH 6.1), and allowed to stand for 20 min at room temperature. Then, the hair is rinsed under tap water, and the towel dry strands are treated with a solution 2 (permanent fixation) and allowed to stand for 10 min. Then, the strands are rinsed under tap water and dried 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	red	2-3
middelblond	red	4
brown	red	5
damaged	red	2-3

Example B53:

2% b.w. of a solution of hydrochinon in water (pH 8; adjusted by ammonia and citric acid) is applied on shampooed hair (blond strand, damaged strand) and then allowed to stand for 10 min. The hair is rinsed and treated with 0.1% b.w. of a solution of the compound of formula (101) in plantaren solution (with pH 6.1) and allowed to stand for 20 min at room temperature. The hair is rinsed under tap water and the towel dry strands treated with a fixating solution (Goldwell) having a pH 3.92 and allowed to stand for 10 min. Then the strands are rinsed under tap water and dried 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	red	2-3
middelblond	red	4
brown	red	5
damaged	red	2-3

Example B54:

Test 1: A solution 1 (permanent lotion; pH 8.2) is applied on shampooed hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 10 min. Then the strands are rinsed under tap water, and the towel dry strands are treated with a 0.1% b.w. colouring material solution of a compound of formula (102) according to example A2, in plantaren and allowed to stand for 20 min. and then rinsed. The towel dry strands are treated with a solution (2) (permanent fixation) and allowed to stand for 10 min. Then the strands are rinsed under tap water and dried for 12 hours at room temperature.

Test 2: Solution (1) (permanent lotion; pH 8.2) is applied on shampooed hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 10 min.. The wet strands are treated with a colouring material solution consisting of a 0.1%, b.w. colouring material solution of the compound of formula (102) in plantaren and allowed to stand for 20 min. and then rinsed. The towel dry strands are treated with solution (2) (permanent fixation) and allowed to stand for 10 min. Then the strands are rinsed under tap water and dried for 12 hours at room temperature.

Test 3: A colouring material consisting of the compound of formula (102) in plantaren is applied on dry hair and then allowed to stand for 20 min., rinsed and dried for 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results			
Strand	Colour (test 1)	Colour (test 2)	Colour (test 3)
blond	violet/	violet/ paler than in test 3	violet
middelblond	violet	violet/ paler than in test 3	violet
damaged	violet	violet/ paler than in test 3	violet
Strand	Washing fastness (test 1)	Washing fastness (test 2)	Washing fastness (test 3)
blond	5	5	3
middelblond	5	5	2
damaged	5	5	2-3

Example B55:

A solution 1 (pH 8.2; permanent lotion) is applied on shampooed hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 10 min. Then the strands are rinsed under tap water and the towel dry strands are treated with a colouring material solution consisting of a compound of formula (102) according to example A2, in plantaren and allowed to stand for 20 min and then rinsed. Then, the towel dry strands are treated with a solution 2 (permanent fixation), and allowed to stand for 10 min. Then, the strands are rinsed under tap water and dried 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	violet	5
middelblond	violet	5
brown	violet	
damaged	violet	5

Example 55B

Application Example 55 is repeated with the difference that instead of a compound of formula (102) according to example A2, a compound of formula (103) according to example A3 is used.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness/Example 55B
blond	blue	5
middelblond	blue	5
brown	blue	
damaged	blue	5

Example 55C

Application Example 56 is repeated with the difference that instead of a compound of formula (102) a compound of formula (106) is used.

Results		
Strand	Colour	Washing fastness/Example 55C
blond	yellow	5
middelblond	yellow	5
brown	yellow	
damaged	yellow	5

Example B56:

Hair (two blond, two middle blond and two damaged hair strands) is treated with a colouring material solution consisting of a 0.1%, b.w. colouring material solution of a compound of formula (102) according to example A2, in plantaren and allowed to stand for 20 min. Then, the strands are rinsed under tap water and dried 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	violet	4
middelblond	violet	4
brown	violet	
damaged	violet	3-4

Example 56B

Application Example 56 is repeated with the difference that instead of a compound of formula (102) a compound of formula (103) is used.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	blue	3
middelblond	blue	3
brown	blue	
damaged	blue	3

Example 56C

Application Example 56 is repeated with the difference that instead of a compound of formula (102) the compound of formula (107) is used .

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness/
blond	yellow	5
middelblond	yellow	5
brown	yellow	

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness/
damaged	yellow	5

Example B57:

A composition comprising

49.95g of a 0.1% b.w. solution of compound of formula (102) according to example A2 in plantaren (pH 6.12), and

0.05g of a 0.1% b.w. solution of ammoniumthioglycolate in water having a pH of 8.0 (the pH is adjusted by ammonia and citric acid),

is applied on shampooed hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 20 min. Then, the hair is rinsed under tap water, and the towel dry strands are treated with a fixating solution (Goldwell) having a pH 3.92 and allowed to stand for 10 min. Then, the strands are rinsed under tap water and dried 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	violet	5
middelblond	violet	4-5
brown	violet	-
damaged	violet	3

Example 57B

Application Example 57 is repeated with the difference that instead of a compound of formula (102) the compound of formula (103) is used.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	blue	2-3
middelblond	blue	2-3
brown	blue	4
damaged	blue	2-3

Example 57C

Application Example 57 is repeated with the difference that instead of the compound of formula (102) the compound of formula (106) is used.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	blue	4
middelblond	blue	4

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
brown	blue	5
damaged	blue	4

Example B58:

Hair (two blond, two middle blond and two damaged hair strands) is treated with a colouring material solution consisting of a 0.1%, b.w. colouring material solution of a compound of formula (102), in plantaren and allowed to stand for 20 min. Then, the strands are rinsed under tap water and dried 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results	
Strand	Colour
blond	blue
middelblond	blue
brown	blue
damaged	blue

Example B60:

A solution 4 (permanent lotion) having a pH 8.7, is applied on shampooed hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 15 min. Then, the strands are rinsed under tap water, and the towel dry strands are treated with a colouring material consisting of a 0.1%, b.w. solution of compound of formula (101) in plantaren and allowed to stand for 20 min. and then rinsed. Then, the towel dry strands are treated with a solution 5 (permanent fixation), and allowed to stand for 10 min. Then the strands are rinsed under tap water and dried 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	blue	5
middelblond	blue	5
brown	blue	5
damaged	blue	5

Example B60:

Hair (two blond, two middle blond and two damaged hair strands) is treated with a colouring material solution consisting of a 0.1%, b.w. solution of compound of formula (107) in plantaren, and allowed to stand for 20 min. Then, the strands are rinsed under tap water and dried 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	blue	Shading:Blue-green
middelblond	blue	3
brown	blue	-
damaged	blue	4

Example B61:

A solution 1 (permanent lotion), having a pH 8.2, is applied on shampooed hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 15 min.. Then the strands are rinsed under tap water, and the towel dry strands are treated with a colouring material consisting of a 0.1% b.w. solution of compound of formula (101) in plantaren and allowed to stand for 20 min. and then rinsed. Then, the towel dry strands are treated with a solution 2 (permanent fixation), and allowed to stand for 10 min. Then, the strands are rinsed under tap water and dried 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	blue	4-5
middelblond	blue	4
brown	blue	5
damaged	blue	4

Example B62:

A composition comprising

49.95g of a 0.1% b.w. solution of compound of formula (107) and

0.05g of a 0.1% b.w. solution of ammonium thioglycolate in water having a pH of 8.0 (the pH is adjusted by ammonia and citric acid),

is applied on shampooed hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 20 min. Then, the hair is rinsed under tap water, and the towel dry strands are treated with a solution 2 (permanent fixation), and allowed to stand for 10 min. Then, the strands are rinsed under tap water and dried 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	violet	5
middelblond	violet	4-5
brown	violet	-
damaged	violet	3

Example B63:

30g of a 0.1% b.w. solution of compound of formula (101) in plantaren and ethanolamin (pH 10),

are applied on dry hair (two blond, two middle blond and two damaged and one blond curled hair strands) and allowed to stand for 20 min. Then, the hair is rinsed under tap water, and dried 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	red	4
middelblond	red	4-5
brown	red	5
damaged	red	3-4
blond curled	red	--

Example B64:

A composition comprising

15g of a 0.1% b.w. solution of compound of formula (103) and

50g of a 0.1% b.w. solution of compound of formula (106) according to example A6 in water,

are applied on dry hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 20 min. Then, the hair is rinsed under tap water, and dried 12 hours at room temperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	green	4
middelblond	green	4-5
brown	green	5
damaged	green	3-4

Example B65:

A solution 4 (permanent lotion) having a pH 8.7, is applied on shampooed hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 15 min. Then, the strands are rinsed under tap water, and the towel dry strands are treated with a colouring material consisting of a 0.1%, b.w. solution of compound of formula (101) according to example A1, in water and allowed to stand for 20 min. and then rinsed. Then, the towel dry strands are treated with a solution 5 (permanent fixation), and allowed to stand for 10 min. Then, the strands are rinsed under tap water, and then shampooed.

Then, a solution 4 (permanent lotion) having a pH 8.7, is applied on the shampooed hair (two blond, two middle blond and two damaged hair strands) and allowed to stand for 15 min.

Then, the strands are rinsed under tap water, and the towel dry strands are treated with a colouring material comprising

15 g of a 0.1%, b.w. solution of compound of formula (103) in water, and

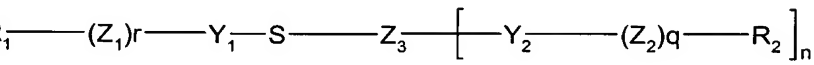
50 g of a 0.1%, b.w. solution of compound of formula (106), in water

and allowed to stand for 20 min. and then rinsed. Then, the towel dry strands are treated with a solution 5 (permanent fixation), and allowed to stand for 10 min. Then the strands are rinsed under tap water, and dried for 12 hours at roomtemperature.

Washing fastness: 10 x washed with shampoo / Results		
Strand	Colour	Washing fastness
blond	red-brown	5
middelblond	red	5
brown	red	5
damaged	red	5

Claims:

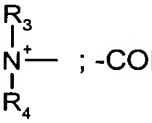
1. Method of dyeing keratin-containing fibers comprising treating the fiber with at least one sulfide dye of formula

(1)  , wherein

R_1 and R_2 each independently from each other are a residue of an organic dye;

Y_1 and Y_2 each independently from each other are unsubstituted or substituted, straight-chain or branched, interrupted or uninterrupted -C_1-C_{10}alkylene-; –C_5-C_{10}cycloalkylene-; C_5-C_{10}arylene; or-C_5-C_{10}arylene-(C_1-C_{10}alkylene)-;

Z_1 and Z_2 independently from each other are –C(O)-; -C_2-C_{12}alkenylene-; -$(CH_2CH_2-O)_{1-5}$-; -C_1-C_{10}alkylene(C_5-C_{10}arylene)-; –C_5-C_{10}arylene-; –C_5-C_{10}cycloalkylene-; -C(O)O-;

-OCO-; -N(R_3)-;  ; -CON(R_4)-; -(R_5)NC(O)-; –O-; -S-; -S(O)-; or –$S(O)_2$-;

R_3, R_4 and R_5 are each independently from each other hydrogen; or unsubstituted or substituted, straight-chain or branched, monocyclic or polycyclic, interrupted or uninterrupted C_1-C_{14}alkyl; C_2-C_{14}alkenyl; C_6-C_{10}aryl; C_6-C_{10}aryl-C_1-C_{10}alkyl; or C_5-C_{10}alkyl(C_5-C_{10}aryl);

r, q and n independently from each other are 0 or 1,

if n is 0,

Z_3 is hydrogen; and

if n is 1,

Z_3 is –S-;

with the proviso that the method does not comprise treating the fiber with an enzyme of the type of a protein disulfidisomerase (EC 5.3.4.1).

2. Method according to claim 1, wherein

Y_1 and Y_2 are unsubstituted or substituted straight-chain or branched, interrupted or uninterrupted –C_5-C_{10}cycloalkylene-; or -C_1-C_{10}alkylene.

3. Method according to claim 1 or 2, wherein

n is 1.

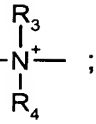
4. Method according to claim 1 or 2, wherein

n is 0.

5. Method according to any of claims 1 to 4, wherein

R_1 and R_2 are identical.

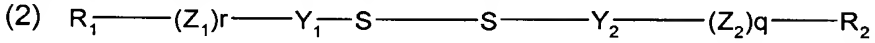
6. Method according to any of claims 1 to 4, wherein

Z_1 and Z_2 independently from each are other -N(R_3)-;  ; -CON(R_4)-; -(R_5)NC(O)-; -O-;

or -S-; and

R_3, R_4 or R_5 are defined as in claim 1.

7. Method according to any claims 1 to 6, wherein at least one sulfide dye of formula

(2) 

and/or at least one sulfide dye of formula

(3) 

is used, wherein

R_1, R_2, Z_1, Z_2, Y_1, Y_2, r and q are defined in claim 1.

8. Method according to any of claims 1 to 8, wherein R_1 and R_2 are selected from the group of anionic, cationic, neutral, amphoter and zwitterionic dyes.

9. Method according to any of claims 1 to 8, wherein R_1 and R_2 are selected from the group of cationic dyes.

10. Method according to any of claims 1 to 8, wherein R_1 and R_2 are selected from the group of anthraquinone, acridine dye, azo, azomethine, hydrazomethine, benzodifuranone, coumarine, diketopyrrolopyrrol, dioxaxine, diphenylmethane, formazane, indigoid, indophenol, naphtalimide, naphthaquinone, nitroaryl, merocyanine, methine, oxazine, perinone, perylene, pyrenequinone, phtalocyanine, phenazine, quinoneimine, quinacridone, quinophtalone, styryl, triphenylmethane, xanthene, thiazine dye and thioxanthene dyes.

11. Method according to claim 10, wherein R_1 and R_2 are selected from azo, azomethine, hydrazomethine, merocyanine, methine and styryl dyes.

12. Method according to any of claims 1 to 11, wherein R_1 and R_2 are selected from azo, azomethine and hydrazomethin dyes.

13. Method according to any of claims 1 to 12 comprising treating the keratin-containing fiber with at least one sulfide dye selected from the dyes of formula

(7) $D^+\text{-}Z_4\text{-}M\text{-}(Z_1)_r\text{-}Y_1\text{-}S\text{-}Z_3\text{-}\left[Y_2\text{-}(Z_2)_q\text{-}M\text{-}Z_5\text{-}D^+\right]_n$; and

(8) $T\text{-}Z_4\text{-}Q^+\text{-}(Z_1)_r\text{-}Y_1\text{-}S\text{-}Z_3\text{-}\left[Y_2\text{-}(Z_2)q\text{-}Q^+\text{-}Z_5\text{-}T\right]_n$; wherein

Z_4 and Z_5 independently from each other are a bivalent radical selected from -N=N-; $-CR_6$=N-; -N=CR_7-; $-NR_8$-N=CR_9-; and $-R_{10}$C=N-NR_{11}-; wherein

R_6, R_7, R_8, R_9, R_{10} and R_{11} independently from each other are hydrogen; unsubstituted or substituted C_1-C_{14}alkyl; C_2-C_{14}alkenyl; C_5-C_{10}aryl; C_1 C_{10}alkyl-C_5-C_{10}aryl; or C_5-C_{10}aryl-C_1-C_{10}alkyl; and

D^+ is a cationic radical of a substituted or unsubstituted aromatic or heterocyclic compound, wherein the cationic charge may be part of the aromatic compounds or part of the substituent;

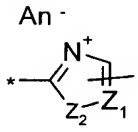
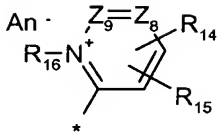
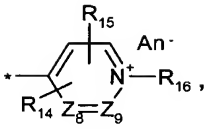
M is a bivalent radical of an aromatic or heteroaromatic substituted or unsubstituted compound;

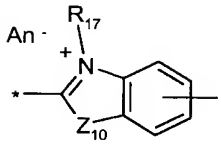
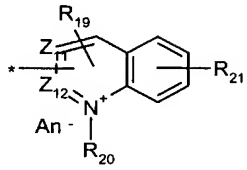
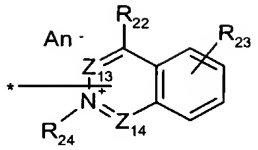
T is a radical of an aromatic substituted or unsubstituted compound;

Q^+ is a cationic biradical of a substituted or unsubstituted aromnatic or heteroaromatic compound; and

Z_1, Z_2, Z_3, Y_1, Y_2, n, r and q are defined as in claim 1.

14. Method according to claim 13, wherein D^+ is selected from a radical of a cationic aromatic heterocyclic compound of the formulae

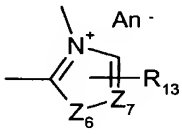
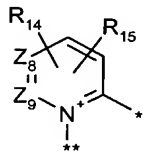
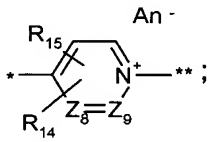
(9)  ; (10)  , (10')  ,

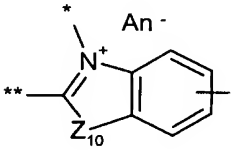
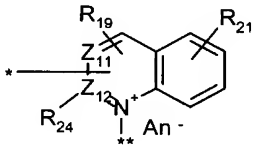
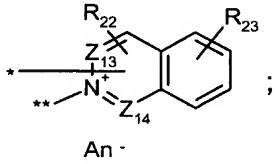
(11)  , (12)  or (13) 

wherein

the asterix * indicates the bond to Z_4 and/or Z_5 of formula (7); and

Q^+ is a cationic bivalent radical of an aromatic heterocyclic compound of formulae

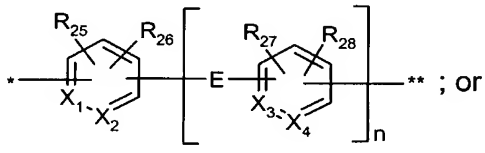
(14)  ; (15)  ; (15')  ;

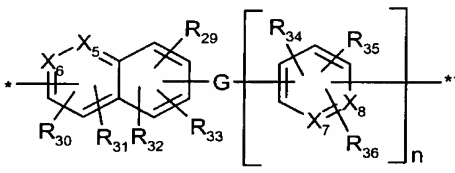
(16)  ; (17)  ; or (18)  ;

wherein

the asterix * indicates a bond to Z_4 and/or Z_5 of formula (8);

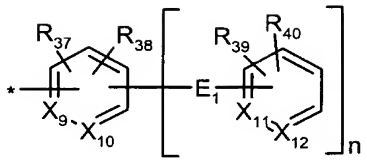
the asterix ** is a bond to Z_1 and/or Z_2 of formula (8); and

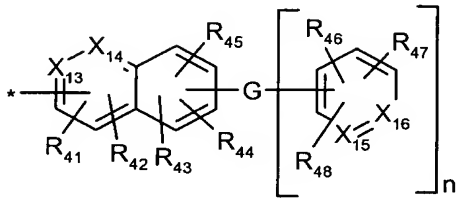
M is a bivalent radical of formulae (19)  ; or

(20)  , wherein

the asterix * indicates the bond to Z_4 or/and Z_5 of formula (7);

the asterix ** indicates the bond to Z_1 and/or Z_2 of formula (7); and

T is a radical of the compounds of formulae (21)  ; or

(22)  , wherein

the asterix * indicates the bond to Z_4 and/or Z_5 of compound of formula (8);

X_1, X_2, X_3, X_4, X_5, X_6, X_7, X_8, X_9, X_{10}, X_{11}, X_{12}, X_{13}, X_{14}, X_{15} and X_{16} are independently from each other N or a radical of CR_{49},

Z_6 is –O-; –S-; or a radical of NR_{50},

Z_7, Z_8, Z_9, Z_{10}, Z_{11}, Z_{12}, Z_{13} and Z_{14} are independently from each other N or a radical of CR_{51};

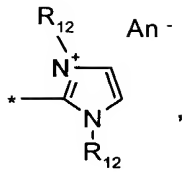
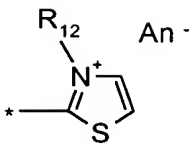
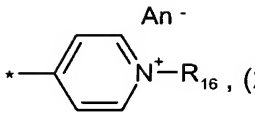
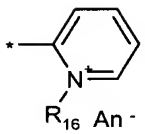
E, E_1, G and G_1 are independently from each other –O-, -S-, -(SO_2)-, -C_1-C_{10}alkylene or -(NR_{52})-;

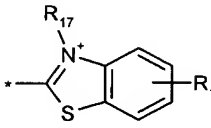
R_{13}, R_{14}, R_{15}, R_{18}, R_{19}, R_{21}, R_{22}, R_{23}, R_{25}, R_{26}, R_{27}, R_{28}, R_{29}, R_{30}, R_{31}, R_{32}, R_{33}, R_{34}, R_{35}, R_{36}, R_{37}, R_{38}, R_{39}, R_{40}, R_{41}, R_{42}, R_{43}, R_{44}, R_{45}, R_{46}, R_{47}, R_{48}, R_{49} and R_{51} are independently from each other hydrogen; halogen; C_1-C_{14}alkyl, which is saturated or unsaturated, linear or branched, substituted or unsubstituted, or interrupted or uninterrupted with heteroatoms; a radical of phenyl, which substituted or unsubstituted; a of carboxylic acid radical; sulfonic acid radical; hydroxy; nitrile; C_1-C_{16}alkoxy, (poly)-hydroxy-C_2-C_4-alkoxy; halogen; sulfonylamino; SR_{60}, NHR_{53}; $NR_{54}R_{55}$; OR_{61}; SO_2; $COOR_{62}$; $NR_{56}COR_{58}$; or $CONR_{57}$; and

R_{12}, R_{16}, R_{17}, R_{20}, R_{24}, R_{50}, R_{52}, R_{53}, R_{54}, R_{55}, R_{56}, R_{57}, R_{58}, R_{60}, R_{61} and R_{62} are each independently of the other hydrogen; unsubstituted or substituted C_1-C_{14}alkyl, C_2-C_{14}alkenyl, C_5-C_{10}aryl, C_5-C_{10}aryl-(C_1-C_{10}alkyl), or -C_1-C_{10}alkyl(C_5-C_{10}aryl); and

An is an anion.

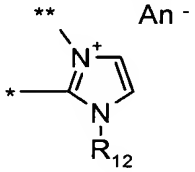
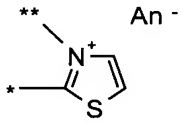
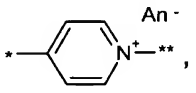
15. Method according to any of precedings claims, wherein D^+ is a radical of a cationic aromatic substituted or unsubstituted heterocyclic compound of formulae

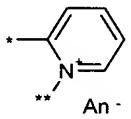
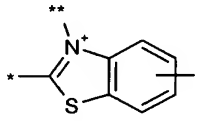
(23)  , (24)  , (25)  , (26)  or

(27)  ; wherein

* is a bond to Z_4 and/or Z_5 of formula (7); and

Q^+ is a biradical of a cationic aromatic substituted or unsubstituted heterocyclic compound

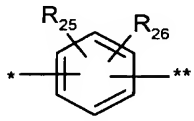
of formulae (28)  , (29)  , (30)  ,

(31)  or (32)  ; wherein

* is a bond to Z_4 and/or Z_5 of formula (8);

** is a bond to and Z_1 and/or Z_2 of formula (8); and

M is a bivalent radical of formula

(33)  , wherein

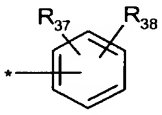
* is a bond to Z_4 and/or Z_5 of formula (7) or (8),

** is a bond to and Z_1 and/or Z_2 of formula (7) or (8); and

n is 1 or 0;

and

T is a radical of formulae

(34)  , wherein

R_{12}, R_{16}, R_{17}, R_{18}, R_{25}, R_{26}, R_{37}, R_{38} and An are defined as in claim 14.

16. A method according to any of claims 1 to 15 wherein the dyeing with the compounds of formula (1) is carried out in the presence of a reduction agent.

17. A method according to claim 16, wherein the reducing agent is selected from thioglycol acid or salts therof, gycerine monothioglycolate, cystein, 2-mercaptopropionic acid, 2-mercaptoethylamine, thiolactic acid, thioglycerine, sodium sulfite, dithionithe, ammonium sulfite, sodium bisulfite, sodium metabisulfite and hydrochinon.

18. A method according to one of claims 1 to 17, comprising treating the keratin-containing fiber

a) optionally with a reduction agent, and

b) at least one single sulfide dye of formula (1) as defined in claim 1, and

c) optionally with an oxidizing agent.

19. A method according to any of the precedings claims, comprising

a. dyeing the keratin-contining fiber with a compound of formula (1),

b wearing the coloured hair for the desired period of time,

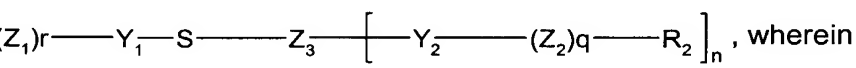
c. removing the colour applied in step a) from hair by contacting the hair with an aqueous based colour removal composition containg a reducing agent capable of disrupting the -S-S-bonds between the dye molecule and the hair fiber surface to cause the dye molcule to become disassociated from the hair fiber.

20. A composition comprising at least one dye of formula (1) as defined in claim 1.

21. A composition according to claim 21 In form of a shampoo, conditioner, gel or emulsion.

22. A composition according to claim 20 or 21 comprising at least one single dye of formula (1) as defined in claim 1, and a direct dye and/or a reactive dye.

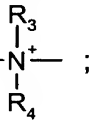
23. Compounds of formula

(1')  , wherein

R_1 and R_2 each independently from each other are a residue of an organic dye;

Y_1 and Y_2 independently from each other are C_1-C_{10}alkylene;

Z_1 and Z_2 independently from each other are –C(O)-; -C_2-C_{12}alkenylene-; -$(CH_2CH_2$-$O)_{1\text{-}5}$-; C_1-C_{10}alkylene(C_5-C_{10}arylene); C_5-C_{10}arylene; C_5-C_{10}cycloalkylene, -C(O)O-, -OCO-;

-N(R_3)-;  ; -CON(R_4)-; -(R_5)NC(O)-; –O- -S-; -S(O)-; or –$S(O)_2$-;

R_3, R_4 and R_5 are each independently from each other hydrogen; C_1-C_{14}alkyl; C_2-C_{14}alkenyl; C_6-C_{10}aryl; C_1-C_5alkyl-C_5-C_{10}aryl; or-C_5-$C_{10}$$C_5$-$C_{10}$aryl;

r, q and n independently from each other are 0; or 1,

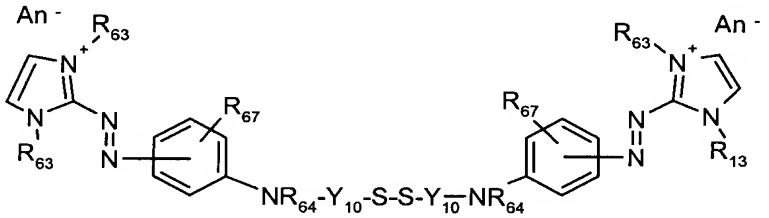
if n is 0,

Z_3 is hydrogen; and

if n is 1,

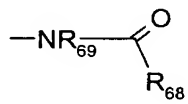
Z_3 is –S-.

24. Compounds of formulae

(35)  , wherein

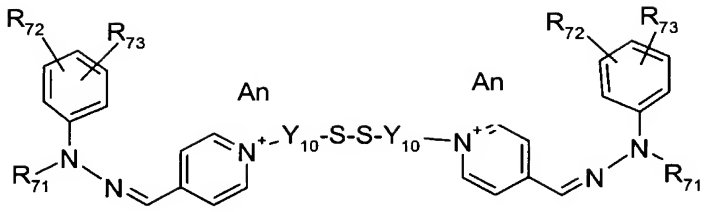
R_{63} is hydrogen; unsubstituted or substituted C_1-C_{14}alkyl; C_5-C_{10}cycloalkyl;C_2-C_{14}alkenyl; C_5-C_{10}aryl-(C_1-C_{10}alkyl); C_1-C_{10}alkyl-(C_5-C_{10}aryl); C_5-C_{10}aryl; and

R_{64} is hydrogen; unsubstituted or substituted, straight-chain or branched, interrupted or uninterrubted C_1-C_{14}alkyl, C_5-C_{10}cycloalkyl, C_5-C_{10}aryl, or C_5-C_{10}aryl-(C_1-C_{10}alkyl); C_1-C_{10}alkyl(C_5-C_{10}aryl);

R_{67} is hydrogen; or a radical of formula (35a)  ;

Y_{10} is unsubstituted or substituted, straight-chain or branched, monocyclic, from C_3-alkyl upwards, or polycyclic, from C_5-alkyl upwards, interrupted or uninterrupted, C_1-C_{10}alkylene; C_5-C_{10}arylene-(C_1-C_{10}alkylene); C_1-C_{10}alkylene-(C_5-C_{10}arylene); or –C_5-C_{10}arylene; and

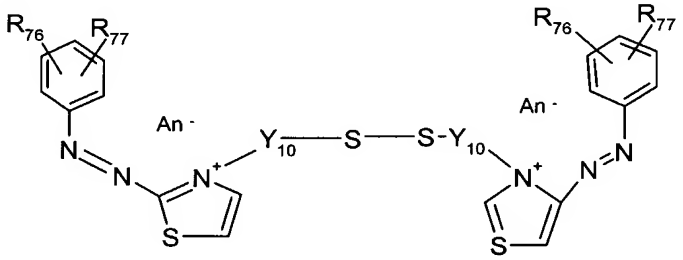
R_{68} and R_{69} are each independently of the other hydrogen, unsubstituted or substituted C_1-C_{14}alkyl, C_2-C_{14}alkenyl, -C_5-C_{10}arylen-(C_1-C_{10}alkyl), -C_1-C_{10}alkylen(C_5-C_{10}aryl), C_5-C_{10}aryl,

(36)  , wherein

R_{71} is hydrogen; unsubstituted or substituted C_1-C_{14}alkyl; C_5-C_{10}cycloalkyl; C_2-C_{14}alkenyl; C_5-C_{10}aryl; C_1-C_{10}alkyl-(C_5-C_{10}aryl); C_5-C_{10}aryl-(C_1-C_{10}alkyl);

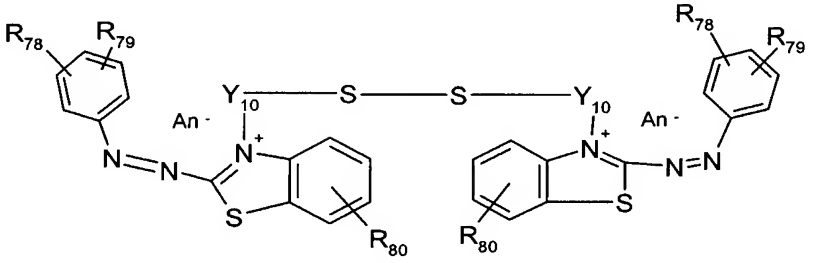
R_{72} and R_{73} are each independently of the other hydrogen; C_1-C_{14}alkyl; C_2-C_{14}alkenyl; a radical of acarboxylic; a radical of a sulfonic acid; C_5-C_{10}aryl, hydroxy, nitril, C_1-C_{16}alkoxy, (poly)-hydroxy-C_2-C_4-alkoxy, carboxylic acid;; halogen; sulfonylamino; SR_{60}; NHR_{53}; $NR_{54}R_{55}$; OR_{61}; $COOR_{62}$; $NR_{56}COR_{58}$; or $CONR_{57}$;

R_{53}, R_{54}, R_{55}, R_{56}, R_{57}, R_{58}, R_{60}, R_{61} and R_{62} are each independently of the other hydrogen; unsubstituted or substituted C_1-C_{14}alkyl; C_2-C_{14}alkenyl; -C_5-C_{10}arylen-(C_1-C_{10}alkyl); -C_1-C_{10}alkylene(C_5-C_{10}aryl); orC_5-C_{10}aryl;

(37)  , wherein

R_{76} and R_{77} are each independently of the other hydrogen, C_1-C_{14}alkyl, which is saturated or unsaturated, linear or branched, substituted or unsubstituted, or interrupted or uninterrupted with heteroatoms; a radical of phenyl, which substituted or unsubstituted; a radical of carboxylic acid; C_5-C_{10}aryl, a radical of hydroxy, nitril, C_1-C_{16}alkoxy, (poly)-hydroxy-C_2-C_4-alkoxy, carboxylic acid, sulfonic acid; halogen, sulfonylamino, SR_{60}, NHR_{53} or $NR_{54}R_{55}$, OR_{61}, SO_2, $COOR_{62}$, $NR_{56}COR_{58}$, $CONR_{57}$;

R_{53}, R_{54}, R_{55}, R_{56}, R_{57}, R_{58}, R_{60}, R_{61} and R_{62} are each independently of the other hydrogen, unsubstituted or substituted C_1-C_{14}alkyl, C_2-C_{14}alkenyl, -C_5-C_{10}aryl-(C_1-C_{10}alkyl), -C_1-C_{10}alkyl(C_5-C_{10}aryl) or C_5-C_{10}aryl;

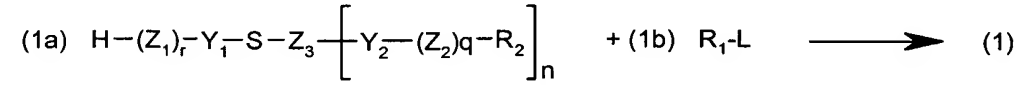
(38)  , wherein

R_{79}, R_{78} and R_{80} are each independently of the other hydrogen; C_1-C_{14}alkyl, which is saturated or unsaturated, linear or branched, substituted or unsubstituted, or interrupted or uninterrupted with heteroatoms; a radical of phenyl, which substituted or unsubstituted; a radical of carboxylic acid; C_5-C_{10}aryl, a radical of hydroxy, nitril, C_1-C_{16}alkoxy, (poly)-hydroxy-C_2-C_4-alkoxy; carboxylic acid; sulfonic acid; halogen; sulfonylamino; SR_{60}; NHR_{53}; $NR_{54}R_{55}$; OR_{61}; SO_2; $COOR_{62}$; $NR_{56}COR_{58}$; or $CONR_{57}$;

R_{53}, R_{54}, R_{55}, R_{56}, R_{57}, R_{58}, R_{60}, R_{61} and R_{62} are each independently of the other hydrogen; unsubstituted or substituted C_1-C_{14}alkyl; C_2-C_{14}alkenyl; C_5-C_{10}arylene-(C_1-C_{10}alkyl), C_1-C_{10}alkylene(C_5-C_{10}aryl), C_5-C_{10}aryl, and

An is an anion.

25. A process for the preparation of compounds of formula (1) according to claim 1, which comprises reacting a compound of formula (1a) with the compound of formula (1b) according to the following reaction scheme:

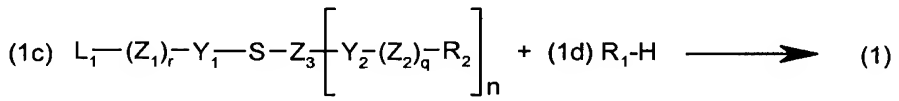


wherein

L is a leaving group; and

R_1, R_2,Y_1, Y_2, Z_2, Z_3, q and r are defined as in claim 1;

27. Process for the preparation of compounds of formula (1) according to claim 1, which comprises reacting a compound of formula (1c) with the compound of formula (1d) according to the following reaction scheme:



wherein L_1 is a leaving group; and

R_1, R_2, Z_1, Z_2, Z_3, Y_1, Y_2, r, q and n are defined as in claim 1.

Application No: GB0506757.4 **Examiner:** Stephen Quick

Claims searched: 1-23, 25-27 and (in part) 24 **Date of search:** 25 July 2005

Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
X	1, 20, 23, 25 & 27 at least	X G H Crawshaw, "Proc. Int. Wool Text. Res. Conf., 8th (1990)", pub. 1990, Wool Res. Organ. N. Z., Christchurch, N. Z., Vol. 4, pages 177-186 & Chemical Abstracts, abstr no 118:170981. D M Lewis & S M Smith, "Reactive dyes and wool damage". See especially references to dye IV on pages IV-179 (paragraphs 2 & 5) and IV-181 (table), and Chemical Abstracts abstract.
X	1, 20, 23, 25 & 27 at least	Journal of the Society of Dyers and Colourists, 1991, Vol. 107(10), pages 357-362 & Chemical Abstracts, abstr no 117:9682. See especially references to dye IV on pages 359 (paragraph 3) and 360 (table 1), and Chemical Abstracts abstract.
X,P	1, 20, 23, 25 & 27 at least	Dyes and Pigments, 1995, Vol. 29(4), pages 275-294 & Chemical Abstracts, abstr no 124:90240. See (for example) section 2.4, table 1 (8th entry) and Chemical Abstracts abstract.
X	20, 23, 25 & 27 at least	WO 2003/099242 A1 (HENKEL) & Chemical Abstracts, abstr no 140:8458. See especially examples 1.1-1.3, 2.1 & 2.2 and Chemical Abstracts abstract.
X	23 at least	Journal of the Society of Dyers and Colourists, 1975, Vol. 91(8), pages 259-264 & Chemical Abstracts, abstr no 83:195191. See (for example) page 264 (paragraph 1 and figure 3) and Chemical Abstracts abstract.

Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC[X] :

Worldwide search of patent documents classified in the following areas of the IPC[07]

The following online and other databases have been used in the preparation of this search report

CAS ONLINE